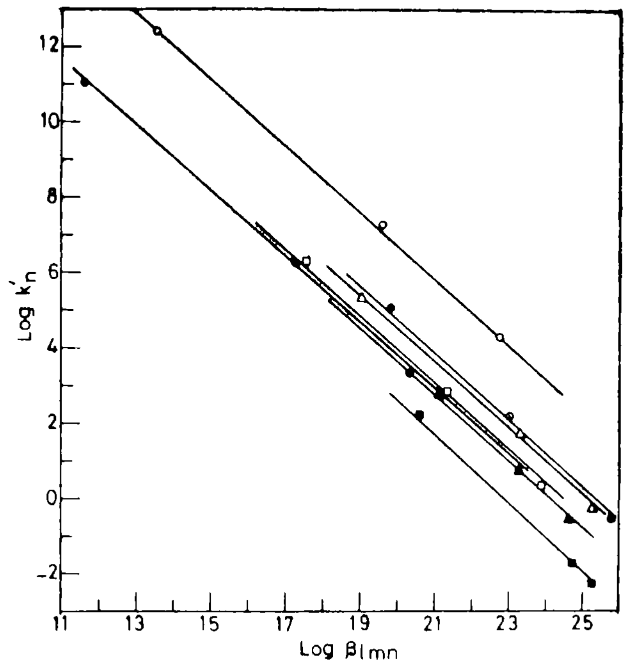

Figure 2. Plot of log k'_n *versus* log β_{lmn} ($k'_n = K_1KD_2k_3$, K_2k_3 or k_3 for fourth order, third order and second order rate constants and β_{lmn} are β_{110}; β_{111} or β_{112} the overall stability constants for intermediates). The different plots are for ○ EDDA, ● NTA, ☐ HPDTA, ■ 1,2-PDTA, △ TMDTA, ▲ DTPA, ○ TTHA.

equality of all slopes appears to be because all reactions follow the same mechanism; while the variation of intercept may be related to the structural pecularities of NiL complexes. Expression (12) reflects this dependence where m is the slope and C is a constant depending upon the particular system under investigation.

$$\log k'_n = m/\log \beta_{lmn} + C \qquad (12)$$

Not enough data is yet available to correlate this constant with structural features of the individual NiL complexes or with ligand itself.

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Transition Metal Chemistry of Oxime-Containing Ligands, Part XI. Copper(II) Complexes of syn-Phenyl-2-pyridylketoxime and syn-Methyl-2-pyridylketoxime

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Summary

Some copper(II) complexes of the types: Cu(HPPK)(PPK)X, Cu(HMPK)(MPK)X (where HPPK = syn-phenyl-2-pyridylketoxime, HMPK = syn-methyl-2-pyridylketoxime and X = Cl^-, Br^-, I^-, NO_3^-, SCN^- or $SeCN^-$) Cu(HPPK)$_2$SO$_4$ · 3H$_2$O and Cu(HMPK)$_2$SO$_4$ · 3H$_2$O were synthesized and characterized by analysis, magnetic susceptibility, e.s.r., reflectance and i.r. spectral measurements. The spectral data suggest that Cu(HPPK)(PPK)X and Cu(HMPK)(MPK)X contain *cis* square-coplanar [Cu(HPPK)(PPK)]$^+$ and [Cu(HMPK)(MPK)]$^+$ units respectively, linked by weakly coordinated anions, giving infinite polymeric highly distorted octahedral chain structures, whereas Cu(HPPK)$_2$SO$_4$ · 3H$_2$O and Cu(HMPK)$_2$SO$_4$ · 3H$_2$O have a *cis* distorted octahedral structure containing two ligand molecules of ketoxime and a bidentate sulphate group. The polycrystalline e.s.r. spectra suggest a distorted octahedral stereochemistry for the Cu^{II} ion involving a $d_{x^2-y^2}$ ground-state. By using e.s.r. and reflectance spectral data, the orbital reduction parameters, $k_{\|}$ and $k_{\perp}$, were calculated and interpreted in terms of molecular orbital coefficients.

Introduction

Although metal complexes of dimethine or α-diimine ligands containing (–N=C–C=N–) as the structural unit have been studied(1) extensively over the past three decades, metal

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complexes of syn-phenyl-2-pyridylketoxime (HPPK) and syn-methyl-2-pyridylketoxime (HMPK) have received[2] very little attention. For copper(II) complexes, studies[3] have been restricted mainly to pyridine-2-aldoxime (HPOX), and 6-methylpyridine-2-aldoxime (HMPX). We have now studied and systematically characterized copper(II) complexes of HPPK and HMPK by magnetic and spectral measurements.

Experimental

syn-Phenyl-2-pyridylketoxime (HPPK) and syn-methyl-2-pyridylketoxime (HMPK) were prepared from 2-benzoylpyridine and 2-acetylpyridine (K & K Laboratories, New York) by the method of Drago *et. al.*[4]. The authenticity of compounds was established by elemental analysis and physical properties (HPPK had m.p. 163–164° (lit. m.p. 163°) and HMPK, m.p. 121–122° (lit. m.p. 121°) and i.r. spectra. The hydrated copper(II) salts, 2,2-dimethoxypropane (K & K Laboratories) and other organic solvents were reagent grade.

Preparation and analysis of complexes

Monohydrogen-bis(syn-phenyl-2-pyridylketoxime)copper(II) halide, Cu(HPPK)(PPK)X, and monohydrogen-bis(syn-methyl-2-pyridylketoxime)copper(II) halide, Cu(HMPK)-(MPK)X (X = Cl or Br)

HPPK or HMPK (1.6 mmol) were dissolved in EtOH (25 cm^3) and 2,2-dimethoxypropane (20 cm^3) and the solution was warmed for 5–10 min at 60° with stirring. A solution of $CuHal_2 \cdot 2\,H_2O$ (0.75 mmol) in EtOH (25 cm^3) was treated in exactly the same manner. Ligand and metal salt solutions were then mixed and boiled under reflux for 30 min. The resulting dark green solution gave a fine dark green polycrystalline solid on cooling at room temperature. The solid was filtered, washed with EtOH and Et_2O and dried over P_4O_{10} *in vacuo.*

Monohydrogen-bis(syn-phenyl-2-pyridylketoxime)copper(II) nitrate, Cu(HPPK)(PPK)NO$_3$ and monohydrogen-bis(syn-methyl-2-pyridylketoxime)copper(II) nitrate, Cu(HMPK)-(MPK)NO$_3$

HPPK or HMPK (1.0 mmol) was dissolved in 1 : 1 EtOH : 2,2-dimethoxypropane (20 cm^3) and the solution was heated for 15 min at 60–65° with stirring. A solution of $Cu(NO_3)_2 \cdot 3\,H_2O$ (0.5 mmol) in the above solvent mixture (25 cm^3) was refluxed for 30 min and added dropwise with stirring to a hot solution of the ligand. The green polycrystalline solid which was obtained immediately, was filtered, washed with EtOH and Et_2O and dried over P_4O_{10} *in vacuo.*

Monohydrogen-bis(syn-phenyl-2-pyridylketoxime)copper(II) iodide, thiocyanate or selenocyanate, Cu(HPPK)(PPK)X and monohydrogen-bis(syn-methyl-2-pyridylketoxime) copper(II) iodide, thiocyanate or selenocyanate, Cu(HMPK)(MPK)X (X = I^-, SCN^- or $SeCN^-$)

A suspension of Cu(HPPK)(PPK)NO$_3$ or Cu(HMPK)-(MPK)NO$_3$ (0.01 mmol) in EtOH (20 cm^3) was treated with solid KI, KSCN or KSeCN (0.01 mmol). Reaction took place immediately and the fine polycrystalline solid which was obtained in each case, was filtered, washed initially with a small amount of H_2O and then with EtOH and Et_2O and dried over P_4O_{10} *in vacuo.*

Dihydrogen-bis(syn-phenyl-2-pyridylketoxime)copper(II) sulphate trihydrate, Cu(HPPK)$_2$SO$_4$ · 3 H$_2$O and dihydrogen-bis(syn-methyl-2-pyridylketoxime)copper(II) sulphate trihydrate, Cu(HMPK)$_2$SO$_4$ · 3 H$_2$O

A solution of HPPK or HMPK (1.0 mmol), dissolved in hot EtOH (20 cm^3), was added dropwise with stirring to a solution of $CuSO_4 \cdot 5\,H_2O$ (0.5 mmol) in H_2O (10 cm^3). The resulting green solution was refluxed for 2 h and then set aside at room temperature for several days. The light green polycrystalline solid which formed gradually was filtered, washed first with H_2O and then with EtOH and Et_2O and dried over P_4O_{10} *in vacuo.*

The copper(II) content in the complexes was estimated iodometrically following standard literature method[5] after destroying the organic residues first with aqua regia and then with conc. H_2SO_4. Halides were determined by Volhard's method[5] and nitrate was determined[5] as its nitrone salt. The carbon, hydrogen and nitrogen analyses results, obtained through the courtesy of the Microanalytical Division, Aligarh Muslim University, Aligarh, are presented in Table 1.

Physicochemical studies

All magnetic susceptibilities were measured on polycrystalline samples with a standard Gouy's balance using

Table 1. Analytical and magnetic data for the copper(II) complexes

Compound	Found (Calcd.) % C	H	N	X	M	U$_{eff}$/298 K (U$_B$)
Cu(HPPK) (PPK)Cl[a]	58.3(58.3)	3.86(3.8)	11.36(11.3)	7.2(7.2)	12.9(12.85)	1.88
Cu(HPPK) (PPK)Br	53.5(53.5)	3.5(3.52)	10.45(10.4)	14.9(14.85)	11.8(11.8)	1.89
Cu(HPPK) (PPK)I	49.2(49.2)	3.27(3.2)	9.6(9.6)	21.7(21.7)	10.8(10.8)	1.91
Cu(HPPK) (PPK)NO$_3$	55.4(55.3)	3.7(3.65)	10.8(10.75)	12.0(11.9)	12.3(12.2)	1.92
Cu(HPPK) (PPK)SCN	58.1(58.1)	3.7(3.7)	13.5(13.55)	–	12.3(12.3)	1.94
Cu(HPPK) (PPK)SeCN	53.2(53.2)	3.42(3.4)	12.4(12.4)	–	11.3(11.3)	1.94
Cu(HPPK)$_2$SO$_4$ · 3 H$_2$O	47.3(47.25)	4.3(4.3)	9.2(9.18)	–	10.4(10.4)	1.88
Cu(HMPK) (MPK)Cl[b]	45.45(45.4)	4.1(4.05)	15.2(15.1)	9.5(9.6)	17.2(17.2)	1.85
Cu(HMPK) (MPK)Br	40.6(40.5)	3.6(3.6)	13.5(13.5)	19.4(19.3)	15.4(15.3)	1.86
Cu(HMPK) (MPK)I	36.4(36.4)	3.3(3.25)	12.15(12.1)	27.55(27.5)	13.8(13.8)	1.89
Cu(HMPK) (MPK)NO$_3$	42.4(42.4)	3.8(3.8)	17.7(17.7)	15.7(15.6)	16.1(16.0)	1.91
Cu(HMPK) (MPK)SCN	42.7(42.6)	3.3(3.3)	18.7(18.6)	–	14.1(14.1)	1.92
Cu(HMPK) (MPK)SeCN	35.3(35.3)	2.8(2.75)	15.5(15.9)	–	11.7(11.7)	1.92
Cu(HMPK)$_2$ SO$_4$ · 3 H$_2$O	34.62(34.6)	4.55(4.5)	11.6(11.5)	–	13.1(13.1)	1.86

[a] HPPK = syn-phenyl-2-pyridylketoxime; [b] HMPK = syn-methyl-2-pyridylketoxime.

Table 2. E.s.r. spectral data and bond parameters for copper(II) complexes

Compound	g_x	g_y	g_z	g(av)	k_{11}[a]	k_1	α	β[b]	β_1[c]
Cu(HPPK) (PPK)Cl	2.0486	2.0600	2.2420	2.1168	0.73–0.80	0.74	0.73–0.80	0.93–1.00	1.00
Cu(HPPK) (PPK)Br	2.0480	2.0693	2.2430	2.1171	0.74–0.81	0.75	0.74–0.81	0.93–1.00	1.00
Cu(HPPK) (PPK)I	2.0500	2.0602	2.2400	2.1167	0.74–0.81	0.76	0.74–0.81	0.94–1.00	1.00
Cu(HPPK) (PPK)NO_3	2.0500	2.0602	2.2406	2.1169	0.75–0.81	0.76	0.75–0.81	0.94–1.00	1.00
Cu(HPPK) (PPK)SCN	2.0480	2.0604	2.2450	2.1178	0.78–0.83	0.77	0.78–0.83	0.93–1.00	1.00
Cu(HPPK) (PPK)SeCN	2.0480	2.0606	2.2480	2.1188	0.79–0.84	0.77	0.79–0.84	0.93–1.00	1.00
$Cu(HPPK)_2SO_4 \cdot 3H_2O$	2.0700	–	2.2974	2.1458	0.77–0.83	0.79	0.77–0.83	0.95–1.00	1.00
Cu(HMPK) (MPK)Cl	2.0540	–	2.2460	2.1180	0.74–0.80	0.74	0.74–0.80	0.93–1.00	1.00
Cu(HMPK) (MPK)Br	2.0535	–	2.2470	2.1180	0.74–0.81	0.74	0.79–0.81	0.93–1.00	1.00
Cu(HMPK) (MPK)I	2.0510	–	2.2450	2.1157	0.74–0.80	0.73	0.74–0.80	0.91–0.97	1.00
Cu(HMPK) (MPK)NO_3	2.0500	–	2.2426	2.1142	0.74–0.81	0.74	0.74–0.81	0.91–0.98	1.00
Cu(HMPK) (MPK)SCN	2.0508	–	2.2517	2.1177	0.79–0.84	0.75	0.79–0.83	0.90–0.95	1.00
Cu(HMPK) (MPK)SeCN	2.0500	–	2.2520	2.1173	0.79–0.84	0.75	0.79–0.83	0.90–0.95	1.00
$Cu(HMPK)_2SO_4 \cdot 3H_2O$	2.0658	–	2.2800	2.1378	0.75–0.80	0.77	0.75–0.77	0.96–1.00	1.00

[a] The values of k_{11} are given as a range of values, as the energies of the $d_{xy} \rightarrow d_{x^2-y^2}$ ($^2B_{1g} \rightarrow {}^2B_{2g}$) can be determined within limits;
[b] the range of β has been cut off at 1.00 since $\beta \leq 1$; [c] $\beta_1 = 1.00$ assumed.

Table 3. Reflectance spectral data for copper(II) complexes (cm^{-1}) at room temperature

Compound	$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2B_{1g} \rightarrow {}^2B_{2g}$[a]	$^2B_{1g} \rightarrow {}^2E_g$
Cu(HPPK) (PPK)Cl	14700	14700–17545	17545
Cu(HPPK) (PPK)Br	14705	14705–17857	17857
Cu(HPPK) (PPK)I	14900	14900–17982	17982
Cu(HPPK) (PPK)NO_3	15400	15400–18182	18182
Cu(HPPK) (PPK)SCN	16670	16670–18890	18890
Cu(HPPK) (PPK)SeCN	16680	16680–18900	18900
$Cu(HPPK)_2SO_4 \cdot 3H_2O$	13200	13200–15200	15200
Cu(HMPK) (MPK)Cl	14710	14700–17550	17550
Cu(HMPK) (MPK)Br	14710	14710–17860	17860
Cu(HMPK) (MPK)I	14900	14900–17970	17970
Cu(HMPK) (MPK)NO_3	15600	15600–18200	18200
Cu(HMPK) (MPK)SCN	16710	16710–18970	18970
Cu(HMPK) (MPK)SeCN	16720	16720–18970	18970
$Cu(HMPK)_2SO_4 \cdot 3H_2O$	13260	13260–15200	15200

[a] This transition is masked by the $^2B_{1g} \rightarrow {}^2E_g$ transition, therefore, the estimated range is given.

$CoHg(NCS)_4$(6) as calibrant. The sample temperatures were measured with a copper-constant thermocouple above 100 K and a platinum resistance thermometer below 100 K. Diamagnetic corrections were made using Pascal's constants(7). The estimated error limits for reported magnetic moments are ± 0.05 U_B. The magnetic moments at 298 K are reported in Table 1. All e.s.r. spectra were recorded on a Varian Spectrometer in solid state as polycrystalline sample using DPPH as a reference material. The e.s.r. spectral data with various parameters are presented in Table 2. The diffuse reflectance spectra of all the complexes were measured on a Cary 14 spectrophotometer equipped with a diffuse reflectance accessory, using MgO as a reference. The data at room temperature are presented in Table 3. The i.r. spectra in the 4000–200 cm^{-1} range of the ligands and their complexes were measured on a Perkin-Elmer 337 spectrophotometer in CsI.

Results and Discussion

The copper(II) ion on interaction with HPPK and HMPK yields complexes corresponding to the general formula Cu(HPPK)(PPK)X, Cu(HMPK)(MPK)X (where X = Cl^-, Br^-, I^-, NO_3^-, SCN^- or $SeCN^-$), $Cu(HPPK)_2SO_4 \cdot 3H_2O$ and $Cu(HMPK)_2SO_4 \cdot 3H_2O$. All these complexes are insoluble in H_2O and common organic polar and nonpolar solvents preventing determination of molecular weight, conductivity and solution electronic spectra. They do not possess sharp m.p's and decompose on heating above 250°. Their insolubility in common organic solvents and nonmelting nature indicate that they are polymeric or ionic.

Magnetic susceptibilities

The copper(II) complexes have room temperature U_{eff} in the 1.94–1.88 U_B range which fall slightly at liquid nitrogen temperature. The Curie-Weiss law is obeyed with negligably small value of θ (Weiss constant). The magnetic moments clearly indicate(8, 9) the presence of one unpaired electron, as expected for copper(II) complexes. The decrease of U_{eff} with decreasing temperature and the slightly higher than spin-only value of the room temperature moment implies the presence of the low-lying excited term which, at high temperature, is able to mix some of its orbital angular momentum with the spin angular momentum of the ground state *via* spin orbit coupling(8, 9). This mixing is quite common for copper(II) complexes with distorted ligand fields(10). The low-symmetry component of the ligand-field also serves to split the ground state. In fact, no significant conclusion can be drawn from the magnetic data exhibited by these copper(II) complexes regarding the stereochemistry.

E.s.r. spectra

The polycrystalline e.s.r. spectra of Cu(HPPK)(PPK)X complexes are characteristic(11) of rhombic symmetry and give three distinct g values whereas Cu(HMPK)(MPK)X, $Cu(HPPK)_2SO_4 \cdot 3H_2O$ and $Cu(HMPK)_2SO_4 \cdot 3H_2O$ complexes exhibit two g values corresponding to a tetragonal ligand field formed by an elongated octahedron. The orbital reduction factors, k_{11} and k_1, which are the measure of the reduction of the spin-orbit coupling constant [$\lambda_0 = 823\ cm^{-1}$ for free copper(II) ion] in these copper(II) complexes are obtained using the expressions(11, 12):

$$g_z = g_{11} = 2.0023 - 8k_{11}^2\lambda_0/E(^2B_{1g} \rightarrow {}^2B_{2g})$$

$$0.5(g_x + g_y) = g_1 = 2.0023 - 2k_1^2\lambda_0/E(^2B_{1g} \rightarrow {}^2E_g)$$

$k_{11} = 0.73$–0.84 and $k_1 = 0.73$–0.77 respectively.

The k_{11} and k_1 parameters have been interpreted variously as purely molecular orbital coefficients and are related(11) by k_{11} = *ca.* $\alpha\beta_1$ and k_1 = *ca.* $\alpha\beta$, where α, β_1 and β are the coefficients of $d_{x^2-y^2}$, d_{xy} and d_{xz}, d_{yz} orbitals in the M'O's to which they contribute; thus α measures σ-bonding, β_1 measures in-plane π-bonding and β measures out-of-plane π-bonding coefficients. By assuming $\beta_1 = 1$ (since HPPK and HMPK have no lone pairs available on the N-atom for bonding with d_{xy}). The value of α and β are calculated for the copper(II) complexes described in this paper. The estimated α coefficient for all the complexes indicate fairly covalent σ-bonding, whereas β coefficients suggest very little bonding of d_{xz}; d_{yz} with the orbitals of the axial anions in these complexes. These results are comparable(11, 13) with those found for $Cu(NH_3)_4X_2$ and $Cu(en)_2X_2$ (en = ethylenediamine) complexes.

Reflectance spectra

The reflectance spectra of Cu(HPPK)(PPK)X and Cu(HMPK)(MPK)X complexes consist of a broad intense absorption band with a maximum in the 17545–18070 cm^{-1} range and a well defined shoulder in the 14700–16720 cm^{-1} range. The spectra are similar to those reported for copper(II) complexes in which the copper(II) ion is either in a square coplanar or octahedral environment with a very large tetragonal distortion(14). For copper(II) ion in a tetragonal environment three principal spectral bands are expected but only few complexes are known(15) in which such bands have been resolved, either by Gaussian analysis or by single crystal polarization studies, and are assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{z^2} \rightarrow d_{x^2-y^2}$); $^2B_{1g} \rightarrow {}^2B_{2g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) and $^2B_{1g} \rightarrow {}^2E_g$ ($d_{xz}, d_{yz} \rightarrow d_{x^2}$–$d_{y^2}$) transitions in order of increasing energy. The low-energy shoulder in the present complexes is assigned(15) to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, this being equal to the splitting of the ^2E_g term. Because the $^2B_{1g} \rightarrow {}^2B_{2g}$ is a low intensity transition, it is generally not observed(15) as a separate band in tetragonally distorted octahedral copper(II) complexes, and hence the main spectral band is assigned(15) to a $^2B_{1g} \rightarrow {}^2E_g$ transition. The splitting of the ^2E_g state is the measure of the difference between the in plane and axial fields and since the in plane field is constant in all the present cases, the change in the position of the bands would be due to the axial field only. In these copper(II) complexes, the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition shifted to higher energy in the order: Cl^- = *ca.* $Br^- < I^- < NO_3^- < SCN^- < SeCN^-$. This, of course, is the decreasing order of tetragonal distortion. Thus the reflectance spectra suggest the square coplanar arrangement of the two ligand molecules around the copper(II) ion as is observed(3) in the pyridine-2-aldoxime (HPOX) and 6-methylpyridine-2-aldoxime (HMPX) copper(II) complexes. The square planar $[Cu(HPPK)(PPK)]^+$ and $[Cu(HMPK)(MPK)]^+$ units, attached to a weakly coordinated anion is evidenced by the dependence of the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition on the anion and i.r. spectra (*vide infra*). Furthermore Cu(HPPK)(PPK)X and Cu(HMPK)(MPK)X complexes have a chain structure with the anion bridging between the square coplanar units; the reflectance spectra are not consistent with those expected for square pyramidal or trigonal bipyramidal structures(11).

The $Cu(HPPK)_2SO_4 \cdot 3H_2O$ and $Cu(HMPK)_2SO_4 \cdot 3H_2O$ complexes exhibit a single sharp band at 15200 cm^{-1} and a weak shoulder at *ca.* 13200 cm^{-1}. The band positions, shape and intensity suggest that copper(II) ion is in the distorted octahedral ligand-field stereochemistry. The i.r. spectra (*vide infra*) do not support the presence of the square coplanar units and the reflectance spectra are inconsistent with those found for a *trans*-octahedral complex. Thus the most probable structure is a *cis*-octahedral with two molecules of ligand ketoxime and with a bidentate sulphate group completing the six coordinate structure.

Infrared spectra

The i.r. spectra of free HPPK and HMPK exhibit the multiple bands over the 3300–2800 cm^{-1} range which are assigned(16) to intermolecular hydrogen bonded OH of the NOH groups. The ν(C–H) stretching vibrations, which could be present in this region, are obscured by ν(OH) absorption bands. The Cu(HPPK) (PPK)X and Cu(HMPK) (MPK)X complexes exhibit the strong broad bands in the 3540–3510; 3440–3420 and 3100–3040 cm^{-1} regions assigned(17) to the free ν(OH), H-bonded OH and ν(C–H) stretching vibrations of the ligand molecules, respectively. None of these complexes exhibits any band in the 3400–3200 cm^{-1} region indicating(3) ionization of the proton of one NOH group of HPPK and HMPK. The $Cu(HPPK)_2SO_4 \cdot 3H_2O$ and $Cu(HMPK)_2SO_4 \cdot 3H_2O$ complexes show a very broad band in the 3600–3200 cm^{-1} region and a sharp band of medium intensity at 3040 cm^{-1} assigned to ν(OH) of free water molecules and ν(C–H) of ligand molecules. The very broad (OH) band of water molecules has obscured the vibrations due to (OH) and H-bonded HO^- groups of ligand molecules.

The free ligands exhibit the ν(C=N) (acyclic) and ν(N–O) at *ca.* 1612 and 980 cm^{-1}, respectively. The ν(C=N) (acyclic) band is shifted towards the low frequency side and obscured by pyridine-Band-I of the ligand molecules in Cu(HPPK)-(PPK)X and Cu(HMPK)(MPK)X complexes. The ν(N–O) band is also shifted towards the low frequency side and appears at *ca.* 1050 cm^{-1}. In $Cu(HPPK)_2SO_4 \cdot 3H_2O$ and $Cu(HMPK)_2SO_4 \cdot 3H_2O$ complexes the ν(C=N) (acyclic) and ν(N–O) bands are observed at *ca.* 1630 and *ca.* 1070 cm^{-1}, respectively. Similar differences have previously been observed(3) in the spectra of metal(II) complexes of HPOX and HMPX. The coordination of pyridine nitrogen atom to the copper(II) atom is indicated by shifting and splitting of the ring vibrations as is usually observed(18) for other metal(II) pyridine complexes.

In nitrato complexes the presence of spectral bands at *ca.* 1350s, *ca.* 1292m and *ca.* 825s cm^{-1} suggest(19) the "semi-coordination" of the nitrate group. The S- or Se-bonded mode of coordination of thiocyanate and selenocyanate group is indicated(20) by the appearence of ν_1[ν(C–N) stretching] at *ca.* 2050vs cm^{-1}. The ν_2[δ(NCS) or δ(NCSe)] and ν_3[ν(C–S) or ν(C–Se)] vibrations are obscured by ligand absorption bands in thiocyanato and selenocyanato complexes. The presence of ν_1 at 990m, ν_2 at 470sh, ν_3 at *ca.* 1070s, *ca.* 1105m and 1155s and ν_4 at *ca.* 610vs, 590vw and 642s cm^{-1} indicate(21) the bidentate coordination of sulphate group in $Cu(HPPK)_2SO_4 \cdot 3H_2O$ and $Cu(HMPK)_2SO_4 \cdot 3H_2O$ complexes.

In the far i.r. region, HPPK and HMPK exhibit the bands at 400s, 335s, *ca.* 290m, *ca.* 275w, *ca.* 250vs and *ca.* 220s cm^{-1} whereas all the copper(II) complexes have absorption bands at 400–385s, 335–330sh, 290–270s, 250–245m and 230–210s cm^{-1} assigned to ligand absorption bands. The Cu(HPPK)(PPK)X and Cu(HMPK)(MPK)X complexes show the bands at 360s and *ca.* 300m cm^{-1} whilst the $Cu(HPPK)_2SO_4 \cdot 3H_2O$ and $Cu(HMPK)_2SO_4 \cdot 3H_2O$ complexes exhibit the bands at 345–340s, 315m and 265–260m cm^{-1} which are assigned to ν(Cu–N, ligand) vibrations.

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Electrochemical and Chemical Reduction Studies of Molybdenum(VI)- and Molybdenum(V)-Ethylenediaminetetraacetic Acid Complexes

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Summary

The electrochemical reduction characteristics of the molybdenum(VI)- and molybdenum(V)-ethylenediaminetetraacetate complexes, $[(MoO_3)_2Y]^{4-}$ and $[Mo_2O_4Y]^{2-}$ respectively have been investigated as a function of pH and free ligand concentration. The nature of chemical reduction of these two complexes with sodium borohydride and sodium dithionite have also been studied in acetate and borate buffers. The electroactive species undergoing electrode reductions have been ascertained by analysing polarograms of the complexes. A mechanism has been proposed to account for the differences observed in the reactivities of these two complexes.

Introduction

Investigation of the electrochemical behavior of molybdenum complexes is of current interest because molybdenum occurs in biological systems. Although polarographic studies on Mo_2^{VI}- and Mo_2^{V}-EDTA complexes have been made previously by several groups of workers(1–4), they have yielded contradictory results. Quite recently Schultz and Sawyer(5), and Ott and Schultz(6) have comprehensively investigated these complexes by cyclic voltammetric, coulometric and chromopotentiometric measurements. The object of the present study was to make a polarographic investigation of these complexes at varying pH and EDTA concentrations in order to characterise the electroactive species undergoing reduction. While the polarographic behavior *vis-a-vis* the cyclovoltammetric feature of the molybdenum-EDTA complexes will assist our understanding the mechanism of electrode reduction(5, 6), another objective of the present work is to investigate the effect of reducing agents, such as sodium borohydride and

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