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NOTE

Anionic Complexes of Nickel(II) and Copper(II) Containing Uni-negative Bidentate Ligands

MS. MINATI SATPATHY and B. PRADHAN*
Department of Chemistry
Regional Engineering College, Rourkela-769 008, India

A series of complexes of the type [M′(BB′)] where M′ = Me_4N^+, $Cepy^+$, M = Ni(II) or Cu(II); BB′ = uni-negative bidentate ligands such as acetylacetone, pyridine carboxylic acid, oxine and diethyldithio-carbamate have been prepared. The nature of bonding and the possible structures of the complexes are discussed. When provided with such an anionic environment, Ni(II) and Cu(II) were found to stabilise octahedral stereochemistry.

Under the present investigation, an attempt has been made to study the preference and stabilization of coordination number and stereochemistry by nickel(II) and copper(II) when provided with N, O, S donor uni-negative bidentate chelates.

All the chemicals used were of AR grade.

An ethanolic solution of tetramethyl ammonium chloride or cetyl pyridinium chloride was mixed with excess of an ethanolic solution of acetyl acetone (ac, ac) picolinic acid (pyca), 8-hydroxy quinoline (ox) or sodium salt of dithiocarbamate (dtc) in 1:3 molar ratio and the resulting solution was added to nickel chloride or copper chloride in ethanol medium with constant stirring. The resulting solution was neturalised with NH_3 solution. The solid products thus formed were separated out and were suction filtered, washed with ethanol, ether and dried in vacuum.

Metal and sulphur were estimated by standard methods.[1] The conductance measurements of *ca.* 10^{-3} M solution in methanol medium were carried out using a Systronics-303 direct reading conductivity meter with a dip type cell. The magnetic susceptibility measurements were carried out at room temperature by a Gouy balance. Diamagnetic corrections were calculated using Pascal's constants.[2] IR spectra were recorded on a Shimadzu-408 and electronic spectra were recorded on Elico-CL-54 spectrophotometers.

The compounds are microcrystalline in nature and are quite stable. They do not possess sharp melting point and decompose above 200°C. The complexes are soluble in methanol. The analytical data (Table-1) revealed a stoichiometry of 1 : 1 : 3. The molar conductance values of *ca.* 10^{-3} $ohm^{-1}cm^2 mol^{-1}$ in methanol medium correspond to 1 : 1 electrolytes.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF METAL COMPLEXES

Compound (colour)	% Analysis, Found (Calcd.)		Λ_m (Ω^{-1}cm^2 mol^{-1})	μ_{eff} (B.M.)
	M	S		
[Cepy][Cu(acac)$_3$] (Bottle green)	9.06 (9.55)	—	100.032	2.3
[Cepy][Cu(pyca)$_3$] (Violet)	8.32 (8.65)	—	100.274	2.2
[Cepy][Cu(ox)$_3$] (Bottle green)	7.50 (7.80)	—	104.020	2.0
[Cepy][Cu(dtc)$_3$] (Black)	7.42 (7.82)	22.9 (23.68)	100.001	2.3
[Me$_4$N][Cu(acac)$_3$] (Yellow)	14.43 (14.61)	—	100.136	2.0
[Me$_4$N][Cu(pyca)$_3$] (Light voilet)	12.32 (12.61)	—	100.729	2.2
[Me$_4$N][Cu(ox)$_3$] (Grey)	10.98 (11.03)	—	106.001	1.8
[Cepy][Ni(acac)$_3$] (Light green)	8.27 (8.89)	—	100.031	3.3
[Cepy][Ni(ox)$_3$] (Yellowish green)	7.02 (7.32)	—	105.621	3.4
[Cepy][Ni(dtc)$_3$] (green)	7.11 (7.26)	23.21 (23.82)	100.314	3.1
[[Me$_4$N][Ni(acac)$_3$] (Bluish white)	13.23 (13.65)	—	100.000	3.4
[Me$_4$N][Ni(ox)$_3$] (Yellowish green)	10.01 (10.20)	—	100.324	3.4

The relevant infrared absorption bands of the complexes with their possible assignments are given in Table-2

The ν(C—N) and ν(C—S) bands due to dithiocarbamates found at *ca.* 1510 cm^{-1} and 1000 cm^{-1}, respectively indicate clearly that they are coordinated to the metal ion as uni-negative bidentate chelate through both the sulphur atoms.[3, 4] The ν(C—O) for oxine obtained at *ca.* 1120 cm^{-1} indicates that it is coordinated to the metal ion in the form of uni-negative bidentate chelate coordinating through nitrogen and oxygen atoms.[5] In the acetylacetonato complexes, the bands due to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ and ν(C—O) were obtained at *ca.* 1610 cm^{-1} and *ca.* 1510 cm^{-1}, respectively, indicating the presence of coordinated uni-negative bidentate acetylacetone group.[6] In case of picolinic acid complexes, the band due to free carboxylic group at *ca.* 1710 cm^{-1} was found to be absent. Other bands due to ν_{asy}(COO) and pyridine rings were found to be present.[7] This suggests that picolinic acid is coordinated to the metal ion as uni-negative bidentate chelate coordinating through oxygen and nitrogen atoms. A sharp band obtained at *ca.* 3050 cm^{-1} in the hexachlorobutadiene mull is assigned to the N—H streching frequency of cetyl-pyridinium complexes.[8] The presence of tetramethyl ammonium group is indicatd by the appearance of bands at *ca.* 940 $cm^{-1}$and 760 cm^{-1} in the complexes.[9]

TABLE-2

KEY IR BANDS (cm^{-1}) OF THE METAL COMPLEXES

Compounds	Acetylacetone		Picolinic acid	Oxine	Dithocarbamate		
	$\nu(C\overset{\cdots}{-})$	$\nu(C—O)$	$\nu_{asym}(CO—O)$	$\nu(C—O)$	$\nu(C—N)$	ν_{asym} (C—S)	$\nu(C—S)$
$[Cepy][Cu(acac)_3]$	1610	1520	—	—	—	—	—
$[Cepy][Cu(pyca)_3$	—	—	1640, 1610	—	—	—	
$[Cepy][Cu(ox)_3]$	—	—	—	1120	—	—	—
$[Cepy][Cu(dtc)_3]$	—	—	—	—	1510	1010	735
$[Me_4N][Cu(acac)_3$	1600	1510	—	—	—	—	—
$[Me_4N][Cu(pyca)_3$	—	—	1640, 1600	—	—	—	
$[Me_4N][Cu(ox)_3]$	—	—	—	1120	—	—	—
$[Cepy][Ni(acac)_3]$	1610	1520	—	—	—	—	—
$[Cepy][Ni(ox)_3]$	—	—	—	1115	—	—	—
$[Cepy][Ni(dtc)_3]$	—	—	—	—	1510	1000	738
$[Me_4N][Ni(acac)_3]$	1610	1515	—	—	—	—	—
$[Me_4N][Ni(ox)_3]$	—	—	—	1120	—	—	—

The electronic spectra are more diagnostic for the coordination number and geometry of the compounds.

The studies of electronic spectra of copper(II) complexes are in consistent with the octahedral nature of the compound. A broad band obtained at *ca.* 15384 cm^{-1} is due to $^3E_g \rightarrow {}^2T_{2g}$ transition for distorted octahedral sterochemistry.

For the hexa-coordinated complexes of Ni(II), the electronic spectral bands are found at *ca.* 12986 cm^{-1}, *ca.* 14492 $cm^{-1}$and *ca.* 22988 cm^{-1}. These may be assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3A_{2g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively. These are in agreement with the octahedral gometry for the complexes.

The magnetc moment values of the copper(II) complexes lie in the range 1.8–2.3 B.M. as expected for octahedral complexes[10] while for the nickel(II) complexes, the values are in the range 3.1–3.4 B.M which is consistent with $3d^8$ configuration.[11]

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