

Studies of Some Co(II), Ni(II) and Cu(II) Complexes with a Mixed Ligand Schiff Base

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Synthesis of mixed ligand Schiff base complexes of general formula of the type $[M(\text{DOSC})_2\text{X}_2]$, where $M = \text{Co(II)}$, Ni(II) and Cu(II) , $\text{DOSC} = 1,2\text{-dimethyl-4-oxoquinazoline semicarbazone}$ and $\text{X} = \text{Cl}^-$, Br^- , I^- , NO_3^- and ClO_4^- . These complexes were characterized by elemental analysis, molar conductance, IR spectra, electronic spectra and magnetic susceptibility. On the basis of above observations the ligand DOSC have been proposed to act in a bidentate manner, coordinating to the metal ion through the nitrogen and oxygen atom of semicarbazone moiety. The remaining coordination sites are occupied by anions such as Cl^- , Br^- , I^- , NO_3^- and ClO_4^- . Electronic spectra and magnetic susceptibility measurements reveal octahedral geometry around the central metal ion. The complexes were found to be non-electrolytic in nature on the basis of low value of molar conductance.

Key Words: Co^{2+} , Ni^{2+} and Cu^{2+} Complexes, 1,2-Dimethyl-4-oxoquinazoline semicarbazone.

INTRODUCTION

Quinazolin derivative is a versatile molecule for designing potential bioactive agents. They have been evaluated for a wide spectrum of biological activities such as anticonvulsant¹, antifungal², antibacterial³⁻⁵, sedative⁶, antiviral^{7,8}, antiHIV^{9,10} and anticancer activities^{11,12}. Keeping the above aspect in mind and in continuation of our earlier work¹³⁻¹⁸ on quinazoline based Schiff bases in the present paper, the synthesis and characterization of a new series of 14 complexes of Co(II), Ni(II) and Cu(II) with 1,2-dimethyl-4-oxoquinazoline semicarbazone (DOSC).

EXPERIMENTAL

All the reagents used were of BDH grade. The metal contents of the complexes were analyzed using standard procedures¹⁹. The IR spectra were recorded on Perkin Elmer-577 spectrophotometer in the frequency region

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4000-200 cm^{-1} . Conductivity measurements made on systronics conductivity meter Model-303 using DMF. Magnetic susceptibility value were measured by Guoy method using mercury tetrathiothiocyanato cobaltate as a calibrant. Electronic spectra were recorded on a Shimadzu 160 A spectrophotometer.

Preparation of DOSC: The ethanolic solution of 1,2-dimethyl-4-oxoquinazoline (1.74 g, 0.01 m) was treated with semicarbazide hydrochloride (1.2 g, 0.01 m) dissolved in 10 % ethanolic solution of sodium acetate. The resulting reaction mixtures were heated on water bath for 3 h when a crystalline colourless solid began to separate. It was heated for further 0.5 h for complete precipitation. It was cooled, filtered, washed with aqueous ethanol dried and crystallized with methyl alcohol as colourless solid was obtained m.p. 236 ± 1 °C, yield *ca.* 60-65 %.

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) have been formed by reacting an ethanolic solutions of metal halides/nitrates/perchlorates in molar ratio 1:2. The resulting reaction mixtures were heated on water bath for 3-4 h. The solid coloured complexes which separated on cooling were filtered, washed with ethanol, dried and recrystallized with methanol and ether and dried in oven. Yield *ca.* 50-55 %.

RESULTS AND DISCUSSION

The analytical and elemental analysis of a series of 14 complexes synthesized are given in Table-1.

The key infrared spectral data of the ligand DOSC and the complexes of the type $[\text{M}(\text{DOSC})_2\text{X}_2]$ are given in Table-2. From the literature²⁰ it is established that semicarbazone ligand can coordinate through azomethine nitrogen and oxygen atoms.

The IR spectra of Schiff base DOSC shows a medium and broad band at 3220 cm^{-1} which may be assigned²¹ to the $\nu(\text{N-H})$ vibrations. This band remain unchanged on complexation indicating non involvement of either terminal amino or secondary amino group in coordination.

Other significant IR band of structural significance in the spectrum of the ligand DOSC appears at 1660 cm^{-1} . This band is sharp and strong may be assigned²² to $\nu(\text{C=O})$ of semicarbazone moiety. The position of this band in all the complexes have been shifted to a higher frequency region at 1700 cm^{-1} with slightly reduced intensity. This shift is undoubtedly due to coordination of the oxygen atom of the carbonyl group to the metal ion. The coordination through oxygen atom of carbonyl group is further confirmed by the appearance of a band at $580\text{-}525 \text{ cm}^{-1}$ in the complexes may be assignable²³ to $\nu(\text{M-O})$.

TABLE-1
COLOUR, ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA,
DECOMPOSITION TEMPERATURE AND CONDUCTIVITY MEASUREMENT
DATA FOR METAL COMPLEXES [M(DOSC)₂X₂]

Compd. / colour	Elemental analysis: Found (Calcd.) %				m.p. (°C)	λ_m^a	μ_{eff} (BM)	λ_{max} electronic (cm ⁻¹)
	M	C	H	N				
DOSC	–	57.24	5.79	30.38	268			
Colourless		(57.14)	(5.62)	(30.30)				
[Co(DOSC) ₂ Cl ₂]	10.78	44.65	4.36	23.73	279	16.7	4.91	9100
Green	(10.95)	(44.59)	(4.39)	(23.65)				13700 19900
[Co(DOSC) ₂ Br ₂]	8.59	38.70	3.85	20.63	252	17.2	5.03	9700 13400
Yellowish green	(8.65)	(38.78)	(3.81)	(20.56)				19300
[Co(DOSC) ₂ I ₂]	7.65	34.13	3.31	18.14	305	17.9	5.11	9800 14100
Greenish brown	(7.60)	(34.07)	(3.35)	(18.07)				19600
[Co(DOSC) ₂ (NO ₃) ₂]	9.17	40.87	4.07	21.75	307	18.3	5.17	9300 13800
Green	(9.13)	(40.93)	(4.03)	(21.70)				19300
[Co(DOSC) ₂ (ClO ₄) ₂]	8.23	36.60	3.65	19.53	242	18.7	5.20	9600 14300
Greenish brown	(8.18)	(36.67)	(3.61)	(19.44)				19000
[Ni(DOSC) ₂ Cl ₂]	9.98	44.69	4.35	23.60	237	19.2	3.05	11400 15800
Greenish brown	(9.92)	(44.61)	(4.39)	(23.66)				23100
[Ni(DOSC) ₂ Br ₂]	8.67	38.84	3.78	20.63	234	27.5	3.11	11800 15600
Reddish brown	(8.62)	(38.79)	(3.82)	(20.57)				23000
[Ni(DOSC) ₂ I ₂]	7.63	34.15	3.31	18.01	261	24.7	3.14	11300 15200
Reddish brown	(7.58)	(34.08)	(3.35)	(18.07)				23600
[Ni(DOSC) ₂ (NO ₃) ₂]	9.14	41.79	3.98	21.78	276	23.2	3.28	11900 15300
Light green	(9.10)	(40.94)	(4.03)	(21.71)				23900
[Ni(DOSC) ₂ (ClO ₄) ₂]	8.20	36.59	3.57	19.49	279	22.2	3.24	12100 16200
Green	(8.15)	(36.68)	(3.61)	(19.45)				24100
[Cu(DOSC) ₂ Cl ₂]	10.69	41.32	4.39	23.41	293	14.9	1.92	12700 17600
Dark green	(10.65)	(41.25)	(4.35)	(23.46)				
[Cu(DOSC) ₂ Br ₂]	9.32	38.61	3.74	20.36	301	13.7	1.95	12600 17200
Grayish brown	(9.27)	(38.52)	(3.79)	(20.42)				
[Cu(DOSC) ₂ (NO ₃) ₂]	9.71	21.63	3.96	21.63	312	15.6	1.89	12800 17700
Bluish green	(9.78)	(21.55)	(4.00)	(21.55)				
[Cu(DOSC) ₂ (ClO ₄) ₂]	8.71	36.50	3.54	19.21	319	16.1	1.88	12300 17100
Deep green	(8.76)	(36.43)	(3.58)	(19.32)				

a = molar conductance ohm⁻¹ cm² mol⁻¹

The IR spectrum of the ligand DOSC shows a broad band of medium intensity at 1480 cm⁻¹ which can be assigned²⁴ to $\nu(\text{C}=\text{N})$. In the spectra of the complexes this band shows red shift appearing at 1450-1460 cm⁻¹ clearly indicating coordination of the N atom of azomethine group of semicarbazone moiety. The coordination through azomethine nitrogen is further confirmed by the appearance of a band at 425-390 cm⁻¹ in the complexes may be assignable²⁵ to $\nu(\text{M}-\text{N})$.

TABLE-2
KEY IR SPECTRAL DATA (cm^{-1}) OF 1,2-DIMETHYL-4-OXOQUINAZOLINE
SEMICARBAZONE (DO SC) AND THEIR METAL COMPLEXES

Compd.	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-X})$
DO SC	3220 m,b	1660 s,b	1480 s,m	–	–	–
$[\text{Co}(\text{DO SC})_2\text{Cl}_2]$	3220 m,b	1700 m,b	1450 m,b	570 m	425 m	315 m
$[\text{Co}(\text{DO SC})_2\text{Br}_2]$	3220 m,b	1710 m,b	1460 m,b	565 m	420 m	305 m
$[\text{Co}(\text{DO SC})_2\text{I}_2]$	3220 m,b	1700 m,b	1455 m,b	550 m	410 m	300 m
$[\text{Co}(\text{DO SC})_2(\text{NO}_3)_2]$	3220 m,b	1700 m,b	1460 m,b	550 m	405 m	–
$[\text{Co}(\text{DO SC})_2(\text{ClO}_4)_2]$	3220 m,b	1705 m,b	1450 m,b	555 m	400 m	–
$[\text{Ni}(\text{DO SC})_2\text{Cl}_2]$	3220 m,b	1705 m,b	1455 m,b	535 m	430 m	325 m
$[\text{Ni}(\text{DO SC})_2\text{Br}_2]$	3220 m,b	1700 m,b	1450 m,b	525 m	405 m	295 m
$[\text{Ni}(\text{DO SC})_2\text{I}_2]$	3220 m,b	1710 m,b	1460 m,b	565 m	420 m	265 m
$[\text{Ni}(\text{DO SC})_2(\text{NO}_3)_2]$	3220 m,b	1700 m,b	1455 m,b	580 m	390 m	–
$[\text{Ni}(\text{DO SC})_2(\text{ClO}_4)_2]$	3220 m,b	1710 m,b	1450 m,b	555 m	400 m	–
$[\text{Cu}(\text{DO SC})_2\text{Cl}_2]$	3220 m,b	1700 m,b	1450 m,b	570 m	425 m	315 m
$[\text{Cu}(\text{DO SC})_2\text{Br}_2]$	3220 m,b	1710 m,b	1460 m,b	565 m	420 m	305 m
$[\text{Cu}(\text{DO SC})_2(\text{NO}_3)_2]$	3220 m,b	1700 m,b	1455 m,b	550 m	410 m	–
$[\text{Ni}(\text{DO SC})_2(\text{ClO}_4)_2]$	3220 m,b	1705 m,b	1450 m,b	555 m	400 m	–

The coordination through halogen atoms are indicated by the appearance of a band in the far infrared region between $325\text{-}255\text{ cm}^{-1}$, which may be assigned²⁶ to $\nu(\text{M-X})$ ($\text{X} = \text{Cl}^-$ or Br^-). The evidence of metal halogen is further confirmed on the basis of low value of molar conductance of the complexes in the range of $12.7\text{-}27.5\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$.

The above discussions suggest the Schiff base DO SC to coordinate in a bidentate manner through azomethine nitrogen atom and oxygen atom of semicarbazone moiety. The remaining coordination centers are occupied by Cl^- , Br^- , I^- , NO_3^- and ClO_4^- .

Electronic spectra and magnetic moment data

Electronic spectra of the complexes have been recorded in the region $10,000\text{-}25,000\text{ cm}^{-1}$. The Co(II) complexes display three bands in the regions, $9900\text{-}9000$, $14400\text{-}13500$ and $19900\text{-}19000\text{ cm}^{-1}$ which may be assigned to ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$, ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$, ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ transition, respectively which indicate octahedral²⁷ geometry of the complexes. The proposed geometry of Co(II) complexes is further confirmed^{28,29} by high magnetic moment value in the region $4.9\text{-}5.2\text{ BM}$. The electronic spectra of all the Ni(II) complexes shows three sharp and broad absorptions in the regions, $12200\text{-}11200\text{ cm}^{-1}$, $16200\text{-}15100\text{ cm}^{-1}$ and third one, in the region above 23000 cm^{-1} which may be assigned to ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ and ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ transition, respectively. The appearance of these bands suggest octahedral geometry²⁷ of the complexes. The octahedral geometry of Ni(II) complexes is further confirmed^{28,29} by

the magnetic moment value in the range 3.05-3.28 BM. The Cu(II) complexes shows two broad bands one in the region 17700-17000 cm^{-1} and another in the region 12800-12100 cm^{-1} which suggest octahedral geometry of Cu(II) complexes. This is further confirmed by the magnetic moment value in the range 1.88-1.95 BM for all the Cu(II) complexes.

Conductivity measurement

Conductivity measurements made on systronics conductivity meter model-303 using dimethylformamide as a solvent. The value found to be in the range 22.7-27.5 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating the complexes to be non electrolytic³⁰ in nature.

Hence on the basis of elemental analysis, infrared spectra, decomposition temperature, electronic spectra, magnetic moment and conductivity measurements value the ligand 1,2-dimethyl-4-oxoquinazoline semicarbazone acts in a bidentate manner and coordination takes place through azomethine nitrogen and oxygen atom of semicarbazone moiety. The remaining coordination sites are occupied by Cl^- , Br^- , I^- , NO_3^- and ClO_4^- and the geometry of complexes were proposed to be octahedral in nature as shown in Fig. 1.

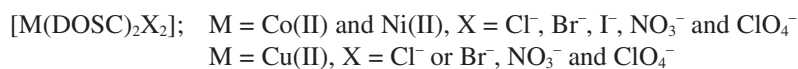
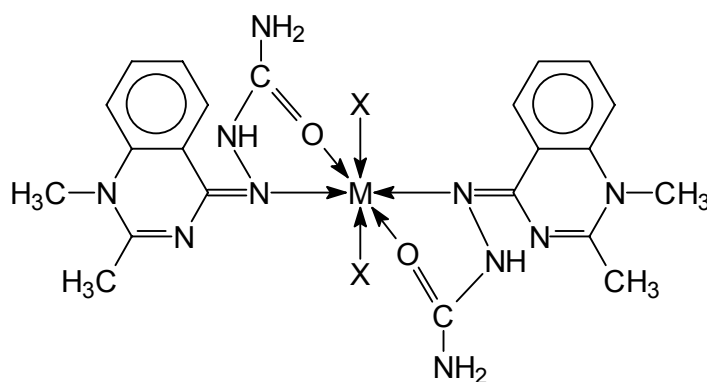


Fig. 1.

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