

Synthesis and Physico-Chemical Study of Some Bivalent Metal Complexes with 1,2-Dimethyl-1,4-Dihydro-4-Oxo-Quinazoline Semicarbazone and Thiosemicarbazone

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The complexes of Co(II), Ni(II) and Cu(II) with 1,2-dimethyl-1,4-dihydro-4-oxo-quinazoline semicarbazone (DMDHOQSC) and 1,2-dimethyl-1,4-dihydro-4-oxo-quinazoline thiosemicarbazone (DMDHOQTSC) have been synthesized and characterised by elemental analysis, molar conductance, magnetic moment, IR and electronic spectra. The ligand DMDHOQSC (L_1) and DMDHOQTSC (L_2) are suggested to behave as neutral tridentate ligands and can coordinate through O, N and S donor sites. The complexes are proposed to be octahedral in geometry.

Key words: Cobalt, nickel, copper, complexes, quinazoline, semicarbazone, thiosemicarbazone.

INTRODUCTION

Various biological activities, such as antiarthritic, anticonvulsant, hypnotic, analgesic¹⁻⁴, antimicrobial⁵ and antiparkinsonian⁶ have been associated with quinazoline derivatives. Since the biological activity of an active ligand is altered many-folds on coordinating with a suitable metal ion^{7, 8}, keeping the above facts in mind and in continuation of our earlier research work⁹⁻¹¹ on transition metal complexes with quinazoline derivatives, in the present paper synthesis and characterisation of Co(II), Ni(II) and Cu(II) complexes with ligands 1,4-dihydro-4-oxo-quinazoline semicarbazone (DMDHOQSC) and 1,4-dihydro-4-oxo-quinazoline thiosemicarbazone (DMDHOQTSC) are reported.

EXPERIMENTAL

All the chemicals used were of BDH quality except 1,2-dimethyl-1,4-dihydro-4-oxoquinazoline which was prepared by arborine, an alkaloid isolated from a plant classified as *Glycosmis arborea correa* (1-methyl-2-benzyl-1,4-dihydro-4-oxoquinazoline). The different methods for the synthesis of arborine have been earlier reported¹²⁻¹⁴. The synthesis of 1,2-dimethyl-1,4-dihydro-4-oxoquinazoline involves three steps in which the first two steps, synthesis of required N-methyl-anthranilamide are the same as those in reported method^{12, 13}. In the final step, N-methylanthranilamide is converted to the corresponding 1,2-dimethyl-1,4-

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dihydro-4-oxoquinazoline by treating it with the required acid chloride in presence of a trace amount of pyridine in benzene

Preparation of the ligand DMDHOQSC (L₁)

1,2-Dimethyl-1,4-dihydro-4-oxoquinazoline dissolved in minimum volume of ethanol was treated with semicarbazide hydrochloride dissolved in 10% ethanolic sodium acetate in the molar ratio 1 : 1. The resulting mixture was heated on a water bath; then a crystalline colourless solid began to separate after 1.5 h. It was heated for a further 30 min for complete precipitation. It was cooled, filtered, washed with aqueous ethanol, dried and recrystallized with dimethyl formamide to furnish a colourless crystalline solid, m.p. 182°C.

Preparation of the ligand DMDHOQTSC (L₂)

1,2-Dimethyl-1,4-dihydro-4-oxoquinazoline dissolved in minimum volume of ethanol was treated with thiosemicarbazide hydrochloride dissolved in 10% alcoholic solution of sodium acetate in the molar ratio 1 : 1. The resulting reaction mixture was heated on a water bath when a crystalline colourless solid began to separate out after 2 h. It was heated for a further 30 min for complete precipitation. It was then cooled, filtered, washed with aqueous ethanol, dried and recrystallised with tetrahydrofuran to obtain a colourless crystalline solid, m.p. 193°C.

Preparation of the complexes

The complexes of Co(II), Ni(II) and Cu(II) were formed by reacting an alcoholic solution of metal halides with ethanolic solutions of ligands DMDHOQSC or DMDHOQTSC in the molar ratio 1 : 2.

The complexes were analysed using standard procedures¹⁵. Carbon, hydrogen and nitrogen were determined by semimicro combustion methods. The IR spectra of the ligands as well as their metal complexes were recorded on Beckman IR-20 spectrophotometer. The UV spectra were recorded on Cary-2390 spectrophotometer. The conductivity measurements were carried out in a Systronics direct reading conductometer 303 using 10⁻³ M DMF solutions. Magnetic moment was determined by Gouy method using mercury tetraisothiocyanato Co(II) as a calibrant. Analytical data, colour, conductivity value, electronic spectra and magnetic moment are recorded in Table-1 and salient features of IR spectral data are recorded in Table-2.

RESULTS AND DISCUSSION

Semicarbazone and thiosemicarbazone ligands can coordinate through oxygen or sulphur atom and $\overset{1}{\text{N}}(\text{>C}=\overset{1}{\text{N}}-\overset{2}{\text{NH}}-(\text{C}=\text{X})-\overset{3}{\text{N}}\text{<})$ of either semicarbazone or thiosemicarbazone moiety¹⁶.

The IR spectra of the ligands L₁ and L₂ observed strong and broad peak in 3260–3200 cm⁻¹ region which can be assigned to $\nu(\text{N-H})$ vibrations¹⁷. In the spectra of the complexes this band remains unaffected indicating non-involve-

TABLE-1
 COLOUR, ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND
 CONDUCTIVITY MEASUREMENT DATA FOR $[M(\text{DMDHOQSC})_2]X_2$ AND
 $[M(\text{DMDHOQTSC})_2]X_2$ COMPLEXES

Compound/ Colour	% Analysis found (Calculated)				λ_{max} electronic cm^{-1}	μ_{eff} (B.M.)	Ω_{max} $\text{ohm}^{-1} \text{cm}^2$ mol^{-1}
	M	C	N	H			
DMDHOQSC(L ¹) Colourless	—	56.89 (57.14)	40.20 (40.30)	5.51 (5.62)	—	—	—
DMDHOQTSC(L ²) Colourless	—	53.28 (53.44)	28.26 (28.34)	5.11 (5.26)	—	—	—
$[\text{Co}(\text{DMDHOQSC})_2]\text{Cl}_2$ Yellowish red	9.76 (9.95)	44.36 (44.59)	23.49 (23.65)	4.27 (4.39)	9930 16730	5.00	116.3
$[\text{Co}(\text{DMDHOQSC})_2]\text{Br}_2$ Green	8.53 (8.65)	38.53 (38.78)	20.44 (20.56)	3.69 (3.81)	9940 16700	5.1	121.4
$[\text{Co}(\text{DMDHOQSC})_2]\text{I}_2$ Brown	7.49 (7.60)	33.83 (34.07)	17.89 (18.07)	3.19 (3.35)	9910 16710	4.8	127.3
$[\text{Co}(\text{DMDHOQTSC})_2]\text{Cl}_2$ Yellowish brown	9.67 (9.44)	42.49 (42.31)	22.27 (22.43)	4.24 (4.16)	9900 16720	4.9	125.4
$[\text{Co}(\text{DMDHOQTSC})_2]\text{Br}_2$ Greenish brown	8.12 (8.27)	36.89 (37.03)	19.45 (19.64)	3.79 (3.64)	9940 16740	4.7	111.7
$[\text{Co}(\text{DMDHOQTSC})_2]\text{I}_2$ Orange	7.34 (7.22)	32.51 (32.72)	17.11 (17.35)	3.09 (3.22)	9935 16720	4.85	121.3
$[\text{Ni}(\text{DMDHOQSC})_2]\text{Cl}_2$ Red	9.79 (9.92)	44.74 (44.61)	23.71 (23.65)	4.46 (4.39)	10730 16220 22610	3.29	118.4
$[\text{Ni}(\text{DMDHOQSC})_2]\text{Br}_2$ Reddish brown	8.74 (8.62)	38.88 (38.79)	20.69 (20.57)	3.89 (3.82)	10720 16200 22600	3.40	112.9
$[\text{Ni}(\text{DMDHOQSC})_2]\text{I}_2$ Violet	7.64 (7.58)	34.31 (34.08)	18.21 (18.07)	3.42 (3.35)	10710 16210 22630	3.35	111.3
$[\text{Ni}(\text{DMDHOQTSC})_2]\text{Cl}_2$ Blue	9.29 (9.41)	42.47 (42.32)	22.53 (22.44)	4.22 (4.16)	10740 16230 22640	3.37	112.4
$[\text{Ni}(\text{DMDHOQTSC})_2]\text{Br}_2$ Green	8.32 (8.23)	36.83 (37.05)	19.79 (19.64)	3.48 (3.64)	10700 16240 22610	3.28	116.7
$[\text{Ni}(\text{DMDHOQTSC})_2]\text{I}_2$ Reddish brown	7.41 (7.27)	32.56 (32.73)	17.49 (17.35)	3.43 (3.22)	10725 16230 22620	3.31	122.3
$[\text{Cu}(\text{DMDHOQSC})_2]\text{Cl}_2$ Steel grey	10.49 (10.65)	44.50 (44.25)	23.63 (23.46)	4.21 (4.35)	14710	1.91	127.3
$[\text{Cu}(\text{DMDHOQSC})_2]\text{Br}_2$ Grey	9.13 (9.27)	38.69 (38.52)	20.27 (20.42)	3.84 (3.79)	14700	1.85	128.4
$[\text{Cu}(\text{DMDHOQTSC})_2]\text{Cl}_2$ Brown	10.23 (10.10)	42.31 (42.00)	22.43 (22.27)	4.24 (4.13)	14710	1.94	130.1
$[\text{Cu}(\text{DMDHOQTSC})_2]\text{Br}_2$ Green	8.94 (8.85)	36.99 (36.80)	19.64 (19.51)	3.45 (3.62)	14720	1.84	128.7

TABLE-2
KEY IR SPECTRAL BANDS OF LIGANDS DMDHOQSC AND DMDHOQTSC AND
THEIR METAL COMPLEXES

Compounds	$\nu(\text{N-H})$	$\nu(\text{C=N})$ (azo- methine)	$\nu(\text{C=N})$ (quina- zalone)	$\nu(\text{C=O})$	$\nu(\text{C=S})$	$\nu(\text{M-O})$	$\nu(\text{M-S})$	$\nu(\text{M-N})$
DMDHOQSC(L ¹)	3260 s, b	1640 m, b	1700 m, b	1760 s	—	—	—	—
DMDHOQTSC(L ²)	3240 s, b	1650 s, b	1710 m, b	—	865 s, s	—	—	—
[Co(DMDHOQSC) ₂]Cl ₂	3255 s, b	1620 m, b	1670 m, b	1740 m, b	—	580 m	—	430 m
[Co(DMDHOQSC) ₂]Br ₂	3260 s, b	1610 m, b	1665 m, b	1745 s, s	—	575 m	—	435 m
[Co(DMDHOQSC) ₂]I ₂	3255 s, b	1606 m, b	1660 m, b	1735 s, s	—	570 m	—	425 m
[Co(DMDHOQTSC) ₂]Cl ₂	3245 s, b	1610 m, b	1680 m, b	—	835 s, s	—	480 m	440 m
[Co(DMDHOQTSC) ₂]Br ₂	3240 s, b	1620 m, b	1685 m, b	—	840 s, s	—	490 m	425 m
[Co(DMDHOQTSC) ₂]I ₂	3240 s, b	1625 m, b	1665 m, b	—	825 s, s	—	485 m	430 m
[Ni(DMDHOQSC) ₂]Cl ₂	3265 s, b	1600 m, b	1665 m, b	1735 s, s	—	540 m	—	435 m
[Ni(DMDHOQSC) ₂]Br ₂	3260 s, b	1610 m, b	1670 m, b	1730 s, s	—	550 m	—	420 m
[Ni(DMDHOQSC) ₂]I ₂	3255 s, b	1610 m, b	1660 m, b	1740 s, s	—	560 m	—	435 m
[Ni(DMDHOQTSC) ₂]Cl ₂	3240 s, b	1625 m, b	1670 m, b	—	810 s, s	—	480 m	440 m
[Ni(DMDHOQTSC) ₂]Br ₂	3245 s, b	1615 m, b	1660 m, b	—	800 s, s	—	485 m	435 m
[Ni(DMDHOQTSC) ₂]I ₂	3240 s, b	1620 m, b	1665 m, b	—	820 s, s	—	475 m	425 m
[Cu(DMDHOQSC) ₂]Cl ₂	3255 s, b	1610 m, b	1670 m, b	1720 s, b	—	560 m	—	435 m
[Cu(DMDHOQSC) ₂]Br ₂	3260 s, b	1625 m, b	1660 m, b	1725 s, s	—	535 m	—	440 m
[Cu(DMDHOQSC) ₂]Cl ₂	3235 s, b	1620 m, b	1670 m, b	—	820 s, s	—	485 m	455 m
[Cu(DMDHOQTSC) ₂]Br ₂	3240 s, b	1625 m, b	1665 m, b	—	815 s, s	—	475 m	430 m

s = strong, b = broad, m = medium, s s = strong and sharp

ment of either terminal amino or secondary amino group in coordination. The IR spectra of both the ligands L_1 and L_2 show a broad band of medium intensity at $1700\text{--}1600\text{ cm}^{-1}$ which can be assigned to $\nu(\text{C}=\text{N})$ (azomethine) and $\nu(\text{C}=\text{N})^{18}$ (N^3 of quinazolone ring). In the spectra of the complexes this band shows red shift appearing in the region $1600\text{--}1510\text{ cm}^{-1}$ suggesting coordination of the azomethine nitrogen as well as N atom N^3 of quinazolone nucleus. The spectra of the ligand L_1 show a sharp and strong band at 1760 cm^{-1} , which can be assigned¹⁹ to $\nu(\text{C}=\text{O})$. In the spectra of the complexes this band shows red shift appearing in the region $1740\text{--}1720\text{ cm}^{-1}$ suggesting coordination to take place through oxygen atom of semicarbazone moiety.

The spectra of the ligand L_2 show a sharp and strong band at 860 cm^{-1} which can be assigned to $\nu(\text{C}=\text{S})$. In the spectra of the complexes this band shows red shift appearing in the region $840\text{--}820\text{ cm}^{-1}$ suggesting coordination to take place through thione sulphur²⁰ of thiosemicarbazone moiety.

The coordination through O, N and S donor atoms is further confirmed by the occurrence of three bands in the far infrared region at $580\text{--}540\text{ cm}^{-1}$, $490\text{--}475\text{ cm}^{-1}$, and $440\text{--}420\text{ cm}^{-1}$ are assigned to $\nu(\text{M}\text{--}\text{O})^{21}$, $\nu(\text{M}\text{--}\text{S})^{22}$, $\nu(\text{M}\text{--}\text{N})^{23}$ respectively.

The above observations clearly indicate that the ligands L_1 and L_2 are coordinated as neutral tridentate molecule and bonded to the metal ion through amine and imine nitrogen and oxygen/sulphur donor sites of either semicarbazone or thiosemicarbazone moiety.

Electronic spectra and magnetic moment data

The magnetic moment values of Co(II), Ni(II) and Cu(II) complexes are found to be 4.80–5.10, 3.28–3.40 and 1.84–1.94 B.M. respectively^{24, 25}. The Co(II) exhibit bands at 9900 and 16700 cm^{-1} corresponding to the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{P})$ which corresponding to octahedral range²⁶. The Ni(II) complexes exhibit three bands at 10700 , 16200 and 22600 cm^{-1} corresponding to the transitions ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{P})$ respectively, which correspond to octahedral geometry²⁶ of the Ni(II) complexes. The Cu(II) complexes exhibit broad band at 14700 cm^{-1} which may be assigned to the transition ${}^2\text{E}_g \rightarrow {}^2\text{T}_{1g}$, which correspond to octahedral geometry²⁶ of the Cu(II) complexes. The electronic and magnetic moments data suggest octahedral geometry for the complexes.

Conductivity measurements

Conductivity of the complexes of the type $[\text{M}(\text{L}^{1-2})_2]\text{X}_2$ were measured in the solvent dimethyl formamide and all the complexes were found to be electrolytic²⁷ in nature of 1 : 2 type and conductivity values in the range $110\text{--}130\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$.

Hence on the basis of the above discussion the complexes of Co(II), Ni(II) and Cu(II) of the type $[\text{M}(\text{DMDHOQSC})_2]\text{X}_2$ and $[\text{M}(\text{DMDHOQTSC})_2]\text{X}_2$ can be presumed to have octahedral geometry as shown in Figs. 1 and 2.

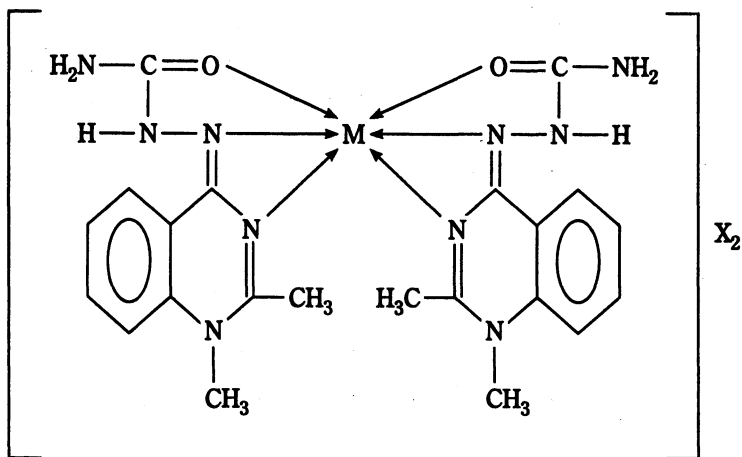


Fig. 1. $[M(DMDHOQSC)_2]X_2$; M = Co(II), Ni(II) and Cu(II); X = Cl⁻, Br⁻ or I⁻

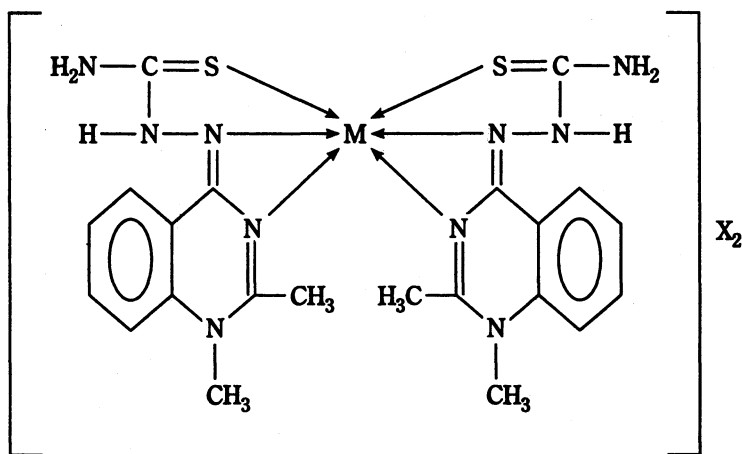


Fig. 2. $[M(DMDHOQTS)_2]X_2$; M = Co(II), Ni(II) and Cu(II); X = Cl⁻, Br⁻ or I⁻

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