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Self Condensation Reaction of Thiosalicylic Acid in the Presence of Some Transition Metal Ions

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A new series of 16-membered tetrathiamacrocyclic complexes have been synthesized by the self-condensation of thiosalicylic acid in the presence of transition metal ions and have been characterized by elemental analyses, IR, ^1H NMR, electronic spectral data, conductivity, and magnetic susceptibility measurements. An octahedral geometry around the metal ion has been suggested for the nickel, cobalt and zinc complexes, while a square-planar geometry is proposed for the copper complexes.

Key Words: 16-Membered tetrathiamacrocyclic complexes, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}.

INTRODUCTION

The possibility of using synthetic macrocycles as models for biological systems has initiated a broad range of research activities, ranging from synthesis of new macrocyclic systems and studies of the properties and functions of macrocyclic ligand complexes to their applications in industry, medicine and other fields[1].

The properties and structures of macrocyclic ligand complexes critically depend on the ring size, number and types of donor atoms as well as on the size and number of chelate rings formed upon coordination[2].

A wide range of macrocyclic polythioethers are known and have been obtained by elegant synthetic routes[3], yet relatively few of these macrocycles have been synthesized by template methods[4–7]. Busch[5, 8–9] was the first to show that thioether macrocyclic ligands effectively bind transition metal ions. One of the best examples of metal ion templates is the self-condensation reaction of *o*-aminobenzaldehyde reported by Busch[10–14]. In the absence of metal ions, the self- condensation reaction is slow and leads to a mixture of polycyclic products which rearrange in the presence of metal ions yielding the desired macrocyclic complexes[12, 13].

Recently, we reported the self-condensation reaction of *o*-aminobenzoic acid in the presence of transition metal ions[15]. We report here the synthesis and characterization of a new series of tetrathiamacrocyclic complexes $[MLX_2]$ (M = Co(II), Ni(II) and Zn(II); X = Cl or NO_3) and $[CuL]X_2$ (X = Cl or NO_3) derived from the self-condensation reaction of thiosalicylic acid in the presence of transition metal ions.

EXPERIMENTAL

The metal salts $CoCl_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$, $ZnCl_2{\cdot}6H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ (all from Aldrich) were the commercially available pure samples. Thiosalicylic acid was also obtained from Aldrich. Solvents were dried before use.

Synthesis of dichloro-nitrato-2,3;6,7;10,11;14,15-tetrabenzo-4,8,12,16-tetra-oxo-1,5,9,13-tetrathiacyclohexadecaneM(II) [MLX_2] [M =Co(II), Ni(II) and Zn(II); X = Cl or NO_3] and 2,3;6,7;10,11;14,15-tetrabenzo-4,8,12,16-tetra-oxo-1,5,9,13-tetrathiacyclohexadecane) copper(II) [CuL]X_2 (X = Cl or NO_3)

Thiosalicylic acid (3.7 g, 24 mmol) dissolved in ethanol (50 mL) was refluxed for about 30 min. A solution of metal salt (6 mmol) in ethanol (40 mL) containing concentrated nitric acid (3–4 drops) was then slowly added. The colour of the solution changed to yellowish-brown. The mixture was stirred and refluxed for a total of 15–18 h. The mixture was left to stand at room temperature for 3 days and then filtered off. The solid product thus formed was washed with ethanol and ether and stored under vacuum.

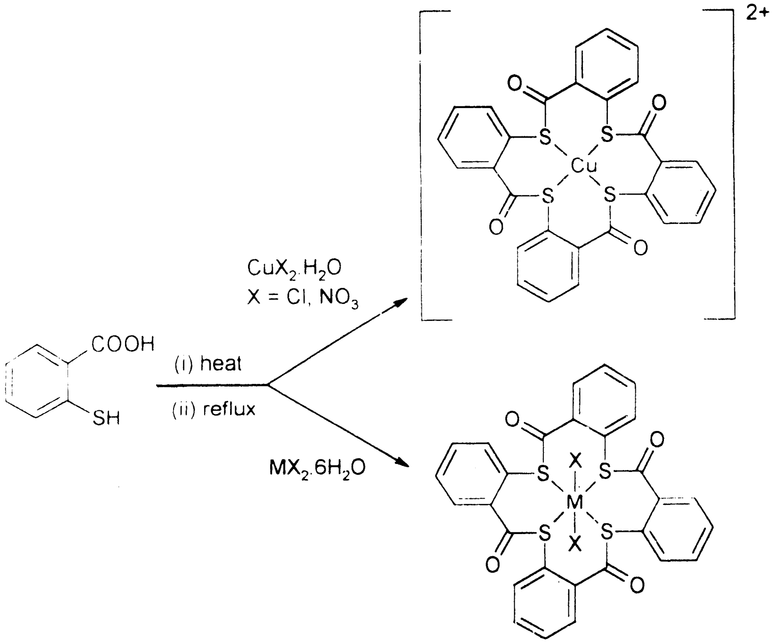
Elemental analyses were obtained from the Microanalytical Laboratory of Al Azhar University, Palestine. Metals were determined by AA-6601F atomic absorption spectrophotometer. IR spectra (4000–400 cm^{-1}) were recorded as KBr discs on a Shimadzu FTIR-8201PC spectrophotometer. ^1H NMR spectra were recorded in DMSO-d_6 using a Jeol JNM-LA300 NMR spectrometer with Me_4Si as internal standard. Electronic spectra of the compounds in DMSO were recorded on a UV-1601 UV-Vis spectrophotometer at room temperature. Magnetic susceptibility measurements were carried out using a Faraday balance at 25°C. The electrical conductivities of 10^{-3} M solutions in DMSO were obtained on an AC13 CM-30V conductivity meter at 25°C.

RESULTS AND DISCUSSION

A new series of 16-membered tetrathiamacrocyclic complexes have been prepared by the self-condensation reaction of thiosalicylic acid in the presence of metal ions (Fig. 1).

It has been observed that the self-condensation required to be initiated several minutes before the metal ions are added. This provides adequate opportunity for the prior formation of the free tetramer, which may then rearrange under the influence of the metal ions.

The products have been characterized, as tetrathiamacrocyclic complexes on the basis of elemental analyses, IR and ^1H NMR spectra. All the complexes have high melting points (>300°C). The results of elemental analyses (Table-1) support the composition of the proposed macrocyclic structure. The yield in all cases is low. All the complexes are freely soluble in H_2O, DMSO and DMF. The purity of all the compounds has been checked by TLC by dissolving the compounds in DMF using ethyl acetate (85%) and methanol (15%) as eluents. The molar conductivity values in DMSO suggested a non-electrolytic nature for all of the complexes except for the copper complexes (Table-1), which are 1 : 2 electrolytes[16]. This clearly demonstrates the fact that both anions in all of the complexes, except those of copper, are coordinated to the metal. However, we could not grow any single crystal suitable for X-ray crystallographic studies.



M = Co(II), Ni(II) and Zn(II)
X = NO_3 or Cl

TABLE-1
YIELDS, COLOURS AND ELEMENTAL ANALYSES OF THE COMPOUNDS

Compound (m.f.)	Yields (%)	Colours	Found (Calcd.) (%)				
			M	C	H	S	N
$[CoLCl_2]$ $(C_{28}H_{16}O_4S_4CoCl_2)$	60	Gray	8.63 (8.74)	49.65 (49.86)	2.35 (2.40)	18.89 (19.01)	—
$[CoL(NO_3)_2]$ $(C_{28}H_{16}N_2O_{10}S_4Co)$	58	Gray	8.00 (8.10)	46.05 (46.23)	2.17 (2.22)	17.52 (17.63)	3.75 (3.85)
$[NiLCl_2]$ $(C_{28}H_{16}O_4S_4NiCl_2)$	63	Light green	8.62 (8.71)	49.66 (49.88)	2.30 (2.40)	18.95 (19.02)	—
$[NiL(NO_3)_2]$ $(C_{28}H_{16}N_2O_{10}S_4Ni)$	67	Light green	7.84 (8.07)	46.05 (46.24)	2.10 (2.22)	17.53 (17.63)	3.77 (3.85)
$[CuL]Cl_2$ $(C_{28}H_{16}O_4S_4CuCl_2)$	60	Green	9.25 (9.36)	49.31 (49.52)	2.25 (2.38)	18.73 (18.88)	—
$[CuL](NO_3)_2$ $(C_{28}H_{16}N_2O_{10}S_4Cu)$	65	Green	8.55 (8.68)	45.78 (45.94)	2.12 (2.21)	17.40 (17.52)	3.79 (3.82)
$[ZnLCl_2]$ $(C_{28}H_{16}O_4S_4ZnCl_2)$	68	Whitish cream	9.49 (9.60)	49.16 (49.39)	2.29 (2.37)	18.70 (18.83)	—
$[ZnL(NO_3)_2]$ $(C_{28}H_{16}N_2O_{10}S_4Zn)$	63	Whitish cream	8.72 (8.91)	45.65 (45.82)	2.15 (2.20)	17.31 (17.47)	3.75 (3.81)

Infrared Spectra

The infrared spectra of all the complexes (Table-2) are similar and suggest the formation of the macrocyclic compounds by the absence of bands characteristic of free SH and OH groups of the starting materials. A strong band appear at 1593–1580 cm^{-1} may be attributable[17] to ν(C=O) adjacent to the sulfur atom. Furthermore, three bands appearing at 1269–1228, 1066–1050, and 899–860 cm^{-1} may reasonably be assigned to asymmetric NO_2 stretching, symmetric stretching and bending modes, respectively. The appearance of these bands in the nitrato complexes of cobalt, nickel and zinc indicates the presence of monodentate coordinated nitrate groups[18]. However, any band around 250 cm^{-1} assignable to ν(M—O) of this group could not be detected as it lies below the range of the instrument used. While in case of copper, the bands at 1254, 1357 and 845 cm^{-1} support the presence of ionic NO_3^-. Bands appearing in the 1456–1407, 1041–1022, and 720–751 cm^{-1} regions are the usual modes of disubstituted benzene.[17]

TABLE-2

IR FREQUENCIES (cm^{-1}) AND MOLAR CONDUCTANCE VALUES OF THE COMPOUNDS

Compound	ν(C=O) (adjacent to S atom)	NO_2 bands	Ring vibrations	Λ_M ($cm^2\ \Omega^{-1}\ mol^{-1}$)
$[CoLCl_2]$	1580 s	—	1407 m, 1038 w, 720 s	20
$[CoL(NO_3)_2]$	1585 s	1269 s, 1066 w, 898 w	1415 m, 1039 w, 742 s	21
$[NiLCl_2]$	1586 s	—	1415 m, 1041 w, 742 s	23
$[NiL(NO_3)_2]$	1586 s	1250 s, 1055 w, 899 w	1417 m, 1037 w, 739 s	19
$[CuL]Cl_2$	1586 s	—	1415 m, 1037 w, 739 s	98
$[CuL](NO_3)_2$	1587 s	1254 s, 1357 s, 845 w	1435 m, 1038 w, 749 s	100
$[ZnLCl_2]$	1593 s	—	1456 m, 1025 w, 751 s	18
$[ZnL(NO_3)_2]$	1587 s	1228 s, 1050 w, 860 w	1417 m, 1022 w, 738 s	20

Abbreviations: s, strong; m, medium; w, weak.

^1H NMR Spectra

The ^1H NMR spectra of both the chloro and nitrato zinc complexes show a broad multiplet in the region 7.08 and 7.20 ppm, respectively, which is assigned to the aromatic ring protons (C_6H_4). However, no bands could be identified for SH and/or OH protons of the starting materials, indicating that the proposed macrocyclic framework has been formed.

Magnetic Moment and Electronic Spectra

The magnetic moment and electronic spectral data of the cobalt, nickel and copper complexes (Table-3) are consistent with the proposed structures.

TABLE-3
MAGNETIC MOMENTS AND UV-VISIBLE SPECTRA OF THE COMPOUNDS

Compound	μ_{eff} (B.M.)	Electronic spectral data λ_{max} (cm^{-1})	Extinction coefficients ε ($dm^3mol^{-1}cm^{-1}$)	Assignments
$[CoLCl_2]$	4.55	14000	92	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
		21900	120	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$[CoL(NO_3)_2]$	4.62	14250	85	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
		22100	115	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$[NiLCl_2]$	3.01	11450	20	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
		17400	50	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
$[NiL(NO_3)_2]$	3.20	11900	25	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
		17700	56	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
$[CuL]Cl_2$	1.76	12900	45	$^2B_{1g} \rightarrow {}^2B_{2g}$
		16000	190	$^2B_{1g} \rightarrow {}^2A_{1g}$
		21500	130	$^2B_{1g} \rightarrow {}^2E_g$
$[CuL](NO_3)_2$	1.74	13250	40	$^2B_{1g} \rightarrow {}^2B_{2g}$
		16100	150	$^2B_{1g} \rightarrow {}^2A_{1g}$
		21650	110	$^2B_{1g} \rightarrow {}^2E_g$

The electronic spectra of the cobalt complexes exhibit absorption in the region 14,250–14,000 and 22,100–21,900 cm^{-1} which may be assigned[19] to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, suggesting an octahedral environment around the cobalt ions. Furthermore, magnetic moments measurements in the range 4.55–4.62 B.M. support the above octahedral geometry.[20] The electronic spectra of the nickel complexes show two distinct bands at 11,900–11,450 cm^{-1} and 17.700–17,400 cm^{-1} which are assigned as $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively, suggesting an octahedral environment around the nickel ions.[19] The observed magnetic moment values in the range 3.01–3.20 B.M. are consistent with the above geometry.[20] The electronic spectra of the copper complexes show three bands in the regions 13,250–12,900, 16,100–16,000 and 21,650–21,500 cm^{-1}, which may be assigned[19] to the $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, corresponding to a square-planar geometry around the copper ions. The magnetic moment measurements in the range 1.74–1.76 B.M. support[20] the square-planar geometry of copper ions.

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