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Synthesis and Stereochemistry of New Cobalt Azo-nitroso Complexes

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Abstract

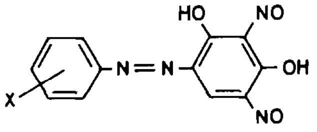
Synthesis and characterization of new cobalt-substituted phenylazo 2,4-dinitrosoresorcinol complexes have been carried out. The analytical data depict the formation of complex compounds with the stoichiometry 2:3 (*o*-COOH, *m*-NO_2) and 1:2 (*o*-Cl, *o*-CH_3, *m*-Cl, *m*-CH_3). All the complexes are of low spin in octahedral and square planar or distorted tetrahedral environments. The octahedral ⇌ tetrahedral equilibria are evident. The complexes in the presence of basic compounds gave some addition products. The electronic transitions and the ligand field parameters are assigned and calculated. The complex formation occurred through the azo group and the phenolic oxygen atom in most complexes. In the *o*-carboxy ligand, the COO^-, –N=N– and the oximic groups participate through complexation.

Introduction

Biological activities and the physiological significance of nitroso compounds have created a great interest in these compounds [1]. The azo compounds have gained much attention because of their use as models in biological systems [2].

In our laboratory, Masoud *et al.* have concentrated on the coordinating behaviour and the chemical equilibria of nitroso [3–16] and azo [17–29] compounds. These compounds possess an ability to form chelates with the transition metal salts. As a continuation of the previous investigations, we now report on ligands containing both functional groups, azo and nitroso, which have not been reported before.

This study is the first report on the synthesis and characterization of some new cobalt complexes derived from substituted phenylazo dinitrosoresorcinol (I) ligands. The investigation was carried out using spectral techniques and magnetic susceptibility measurements to determine the stereochemistry and mode of bonding in the cobalt complexes.



X = o-COOH, o-Cl, o-CH_3, m-Cl, m-CH_3 or m-NO_2

I

Experimental

The ligands were prepared by diazotization of the aniline derivatives (*o*-toluidine, *o*-chloroaniline, anthranilic acid, *m*-toluidine, *m*-chloroaniline and *m*-nitroaniline) followed by coupling with 2,4-dinitrosoresorcinol [30]. All the complexes were prepared in a similar way. 0.025 mol of any ligand was suspended in 50 ml absolute ethanol and mixed with 0.01 mol of the metal chloride salt. The reaction mixture was refluxed with stirring for 6–8 h. On cooling, the complex was filtered off, washed several times with ethanol followed by ether and dried *in vacuo* over P_4O_{10}. The cobalt content was determined by the usual complexometric titration procedure [31]. Carbon, hydrogen, nitrogen and chloride contents were estimated at the Microanalytical Laboratory at Cairo University. The data are collected in Table I. The diffuse reflectance and solution spectra were recorded with a CARY 14 spectrophotometer. The room temperature magnetic measurements were carried out using the Gouy method. The diamagnetic corrections were calculated using Pascal's constant. The solid KBr infrared spectra were made with a Pye Unicam SP 1025.

Results and Discussion

The interaction of hydrated $CoCl_2$ with the entitled ligands in ethanol under reflux afforded the complexes listed in Table. I. They are permanently stable in air and completely soluble in most Lewis bases accompanied by colour changes, which may be associated with geometrical changes and/or the formation of complexes with a higher coordination

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TABLE I. Analytical Data for the Prepared Cobalt Azo-nitroso Complexes[a]

Complex	Found (Calculated) (%)				
	C	H	N	Cl	M
$Co_2(H_2L_1)(L_1)_2(H_2O)$	42.9	2.6	15.5		10.8
	(43.1)	(2.6)	(15.5)		(10.9)
$[Co(L_2)_2]2H_2O$	40.2	2.5	16.0	10.0	8.3
	(40.7)	(2.5)	(15.8)	(10.0)	(8.3)
$Co(L_3)_2$	49.1	3.1	17.7		9.3
	(49.5)	(3.2)	(17.8)		(9.3)
$[Co(L_4)_2]2H_2O$	40.2	2.5	15.9	10.0	8.3
	(40.7)	(2.5)	(15.8)	(10.0)	(8.3)
$[Co(L_5)_2]2H_2O$	46.3	3.6	16.8		8.7
	(46.8)	(3.6)	(16.8)		(8.8)
$[Co_2(L_6)_3]H_2O$	38.9	2.3	18.9		10.6
	(39.1)	(2.3)	(19.0)		(10.7)

[a]Abbreviations: H_2L_1 = o-COOH, HL_2 = o-Cl, HL_3 = o-CH_3, HL_4 = m-Cl, HL_5 = m-CH_3, HL_6 = m-NO_2.

TABLE II. Magnetic and Spectral Data of Bis(*m*-tolyl-azo-2,4-dinitrosoresorcinol)cobalt(II) Dihydrate and Tris(*o*-carboxyphenyl-azo-2,4-dinitrosoresorcinol)dicobalt(II) Monohydrate

Complex	State[a]	μ_{eff}[b] (BM)	Spectral data (cm^{-1})
$Co(L_5)_2(2H_2O)$	solid	1.88	9200 22100
	$C_2H_4Cl_2$		5800 7300 10000 15100 15700 17200 18350
	Py		8600 16970 19120
	α-pic		8680 17000 19050
	β-pic		8800 17340 19340
	γ-pic		8790 17420 19650
	n-but.NH_2		8690 16990 19400
$Co_2(H_2L_1)(L_2)_2(H_2O)$	solid	1.15	9430 21400 44000
	$C_2H_4Cl_2$		6000 7300 10000 15400 16500 17500 18800
	Py		8800 17080 19350
	α-pic		9010 17250 19600
	β-pic		9250 17360 19640
	γ-pic		9300 17480 19660
	n-but.NH_2		8900 17170 19290

[a]Py = pyridine, α-pic = α-picoline, β-pic = β-picoline, γ-pic = γ-picoline, n-but.NH_2 = n-butyl amine. [b]Measured at room temperature.

number. According to the analytical data and the nature of the titled cobalt(II) complexes, the ligands act as monobasic tridentate and/or as bidentate coordinating ligands. The room temperature magnetic moments and the solid reflectance as well as the different solution spectra of the complexes are given in Tables II and III. All the complexes are low spin and could be classified into two series, depending on the electronic requirements of the substituents: (i) $Co(L_5)_2 \cdot 2H_2O$ and $Co_2(H_2L_1)(L_1)_2(H_2O)$ complexes are with μ_{eff} = 1.88 and 1.15 BM/Co^{2+} respectively, and (ii) $Co_2(L_6)_3 \cdot 2H_2O$, $Co(L_2)_2 \cdot 2H_2O$, $Co(L_4)_2 \cdot 2H_2O$ and $Co(L_3)_2$ complexes are with μ_{eff} = 2.70, 2.27, 2.70 and 2.86 BM/Co^{2+}. Class (i) may be associated with a low spin octahedral field and class (ii) is of square planar geometry. The possibility of oxidation of Co(II) to Co(III) in class (i) is experimentally excluded.

The spectra exhibit bands located at 9200, 22100 and 43320 cm^{-1} for $Co(L_5)_2 \cdot 2H_2O$ and 9340, 21400 and 44000 cm^{-1} for the $Co_2(H_2L_1)(L_1)_2(H_2O)$ complex, indicating octahedral spatial configuration. The saturated solution spectra of the $Co(L_5)_2 \cdot 2H_2O$ and $Co_2(H_2L_1)(L_1)_2(H_2O)$ complexes in $C_2H_4Cl_2$

TABLE III. Magnetic and Spectral Data of Cobalt(II) Complexes of *o*-chlorophenyl-azo-, *o*-tolyl-azo-, *m*-chlorophenyl-azo- and *m*-nitrophenyl-azo-2,4-dinitrosoresorcinol

Complex	State[a]	μ_{eff}[b] (BM)	Spectral data (cm^{-1})
$[Co(L_2)_2]2H_2O$	solid	2.27	8400, 19980
	$C_2H_4Cl_2$		8370, 19810
	Py		5200, 12130, 15000, 19300
	α-pic		5350, 11960, 15100, 19580
$Co(L_3)_2$	solid	2.86	8500, 19900
	$C_2H_4Cl_2$		8430, 20000
	Py		5620, 12200, 15200, 19800
	α-pic		5600, 12090, 15200, 19900
$[Co(L_4)_2]2H_2O$	solid	2.70	8420, 20000
	$C_2H_4Cl_2$		8400, 19960
	Py		5220, 12180, 15170, 19440
	α-pic		5400, 11980, 15000, 19600
$[Co_2(L_6)_3]H_2O$	solid	2.70	8450, 20000
	$C_2H_4Cl_2$		8360, 19890
	Py		5200, 11960, 14830, 19380
	α-pic		5300, 12000, 14795, 19670

[a] Py = pyridine, α-pic = α-picoline. [b] Measured at room temperature.

showed a series of bands at 5800, 7300, 10000, 15100, 15700, 17200, 18350 and 42380 cm^{-1} for the first complex and at 6000, 7300, 10000, 15400, 16500, 17500, 18800 and 43320 cm^{-1} for the second complex. These bands typified the presence of equilibria between $T_d \rightleftharpoons O_h$ [32, 33]. The tetrahedral structure may be achieved either by the loss of water and/or the breakdown of certain coordinate bonds of M–L (L = ligand) in the case of the $Co(L_5)_2 \cdot 2H_2O$ complex.

For the *o*-carboxy complex, the data suggest its existence in associated picture through a ligand bridge. The bands located at 5800–10000 and 15400–18880 cm^{-1} are assigned to ν_2 and ν_3, respectively, and the very intense bands around 40000–44000 cm^{-1} could be assigned to the charge transfer transition [34]. The large splitting of the ν_2 and ν_3 bands can be attributed to a large distortion from the ideal tetrahedral symmetry [32, 33] (Table II).

Adduct formation is governed by the ligand field strength of the equatorial ligand and by the steric factor (shape of the ligands and the crystal packing effects). The spectra in pyridine, α-picoline, β-picoline, γ-picoline and n-butylamine are similar with a series of bands in the ranges 8600–9300 (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$; 12800–17980 ($\nu_2$), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and 19050–19690 (ν_3) cm^{-1}), ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. The data are characteristic for Co(II) in an octahedral field [32–34]. According to the geometry and the non-equivalence of the donor atoms of the ligands, the band near 12000 cm^{-1} is expected. The distortion of the crystal field from a regular octahedral symmetry is small based on the non-observed splitting in the spectra [35].

Based on the results of Tanabe and Sugano [36] and Cotton and Goodgame [37], the following equations are applied for the tetrahedral Co(II):

$$\nu_1 = 10\,Dq = \Delta$$

$$\nu_2 = 1.5\Delta + 7.5\bar{B} - Q$$

$$\nu_3 = 1.5\Delta + 7.5\bar{B} + Q$$

$$Q = \frac{1}{2}[(0.6\Delta - 15\,\bar{B})^2 + 0.64\Delta^2]^{1/2}$$

where Δ is the modelus of the ligand field strength and $\bar{B}$ is the effective value of the Racah interelectronic repulsion integral. Each of the three upper states will split by spin–orbit coupling with the splitting in the two T_1 states [38]:

$$T_1 \left\{ \begin{array}{ll} -\frac{9}{4}\lambda' & \left.\right\} \frac{15}{4} \\ +\frac{6}{4}\lambda' & \\ & \left.\right\} \frac{9}{4} \\ +\frac{15}{4}\lambda' & \end{array} \right.$$

The ν_2 and ν_3 spectral bands are the only transitions observed the same as those reported for several tetrahedral Co(II) complexes. Each one of the ν_3

spectral bands consists of three reasonably strong components, one of them is contaminated with that arising from the octahedral one, *ca.* 10 000 cm^{-1}. These components cannot be identified with substrates of the $^4T_1(P)$ level produced by spin–orbit coupling because the separation is too large [39]. The highest energy component is assumed to represent a transition to a doublet state which acquires intensity by spin–orbit coupling interaction with $T_1(P)$ [40]. The middle peaks are assigned to the highest transition and the lowest energy peaks to the unresolved transitions to the two lower energy components of $^4T_1(P)$ [40]. ν_3 is calculated to be 15 650 and 15 270 cm^{-1} for the $Co(L_5)_2 \cdot 2H_2O$ and $Co_2(H_2L_1)(L_1)_2(H_2O)$ complexes, respectively. The ν_2 band is chosen from the three components observed in each spectra produced in the $^4T_1(F)$ state by spin–orbit coupling. The ν_2 values are 6750 and 6527 cm^{-1}, respectively. So, the parameters Δ (10 *Dq*) and $\bar{B}$ could be calculated. The interelectronic repulsion parameter, *B*, ($\beta = \bar{B}/B_0$) was calculated to be 971 cm^{-1} for the free Co(II) ion where $\bar{B} = \nu_2 + \nu_3 - 30Dq/15$. The data are given in Table IV. These values are consistent with those reported for tetrahedral Co(II) complexes [41]. Such values are smaller in the case of the $Co_2(H_2L_1)(L_1)_2(H_2O)$ complex than those of the $Co(L_5)_2 \cdot 2H_2O$ complex, indicating a considerable orbital overlap and delocalization of the d-orbitals of Co(II). This supports a higher covalent character in the second complex than the first one and/or due to the steric effect of the –COOH group. These spectral parameters are in agreement with the mixed nitrogen–oxygen donation [42], lower than those of oxygen and higher than those of nitrogen donations [43].

The room temperature μ_{eff} values of $Co_2(L_6)_3 \cdot H_2O$, $Co(L_2)_2 \cdot 2H_2O$, $Co(L_4)_2 \cdot 2H_2O$ and $Co(L_3)_2$ are 2.70, 2.27, 2.70 and 2.86 BM, respectively. Therefore, a low spin square planar stereochemistry can be assumed for these complexes. The solid reflectance spectra exhibit bands at 8400–8500 cm^{-1} with a narrow band at 20 000 cm^{-1} consistent with a square-planar geometry containing CoN_2O_2 and CoN_4 chromophoras [44] with transitions involving non-bonding rather antibonding orbitals. In a strong field, the ground state of low spin cobalt(II) in a square-planar environment is probably $^2A_{1g}$ with the configuration $e_g^4\ b^2_{2g}\ a_{1g}$. The electronic spectra of these complexes in pyridine or α-picoline exhibit drastic changes in the spectral patterns where bands at 11 960–12 200, 14 720–15 200, 18 850–19 999 cm^{-1} and a strong band at 5200–5620 cm^{-1} appear (Tables II and III). An octahedral configuration for these adducts may be ruled out [32–34]. A five coordinate configuration seems most probable [35] in a trigonal bipyramidal skeleton [45] identified by the presence of four allowed transitions, $^4A_2'(F) \rightarrow {}^4E'(F)$, $^4A_2'(F) \rightarrow {}^4A_2'(P)$, $^4A_2'(F) \rightarrow {}^4E''(P)$, and the lowest energy band to $^4A_2(F) \rightarrow {}^4E(F)$, respectively. It should be noted that the spectra are characterized with high intensity which might be due to an equilibrium between the five coordinate base adducts and the square-planar configuration of the original complex. The infrared spectra of the *o*-tolyl, *m*-tolyl, *o*-chlorophenyl, *m*-chlorophenyl and *m*-nitrophenyl ligands exhibit strong to medium bands in the frequency range 3530–2940 and 960–840 cm^{-1} due to the hydrogen bonded –OH group [3, 4] and the oximic –OH stretching [7, 14]. All ligands exhibit a strong band at 1695–1610 cm^{-1} due to the carbonyl stretching frequency. Such bands together with that at 990–950 cm^{-1} suggest the oxime structure through resonating phenomena [13]. The bands at 1600–1570 cm^{-1} can be attributed to the free azo group [20, 22]. The absence of bands at 1490 cm^{-1} indicate the absence of the nitroso group. Therefore these compounds exist in an azo-oxime structure. On complexation with Co(II): (i) the bands for the carbonyl group are absent; (ii) the azo group is affected on complexation. It is red shifted in some complexes by *ca.* 5–15 cm^{-1} with a decrease in intensity and in others it is blue shifted and appears as a weak band; (iii) in all complexes a broad band at 3490–3160 cm^{-1} is observed. Such a region can be attributed to (a) free –OH, (b) bonded –OH, (c) coordinated water molecules; (iv) in all complexes the bands in the 1490–1400 cm^{-1} region are due to ν(N=O) [7]; (v) the 985–995 cm^{-1} range due to ν(N–O) is absent in all complexes. So all the ligands, except the *o*-carboxy, are coordinated to Co(II) via the azo-nitrogen and the phenolic oxygen atoms. In the $Co_2(H_2L_1)(L_1)(H_2O)$ complex, $\nu(COO^-)$ is absent, indicating the participation of the carboxylate group. ν(–N=N–) is blue shifted by *ca.* 40 cm^{-1} indicating that the azo group coordinates to Co(II). The medium band at 1085 cm^{-1} is due to the coordinated N–O stretching vibration [22]. The strong band at 870 cm^{-1} in the free ligand becomes a weak future at 900 cm^{-1} on complexation suggesting that the oxime group is participating in the coordination. It is therefore suggested that the tridentate behaviour for this ligand is to react with Co(II) through the functional groups: $-COO^-$, –N=N– and =NOH.

TABLE IV. Ligand Field Parameters of T_d Cobalt(II) in $C_2H_4Cl_2$ Solvent

Complex	ν_2	ν_3	10*Dq*	*B'*	β
$Co(L_5)_2 \cdot 2H_2O$	6750	15650	3886	716	0.74
$Co_2(H_2L_1)(L_1)_2 \cdot H_2O$	6527	15270	3757	702	0.72

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