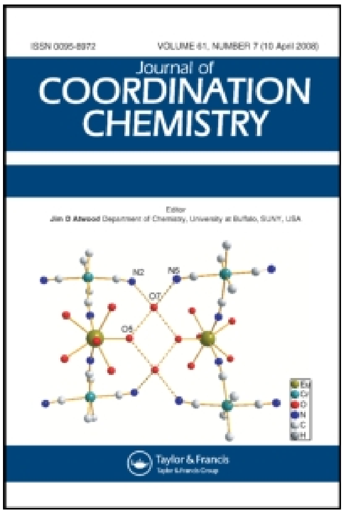

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SYNTHESIS AND SPECTROSCOPIC STUDY OF COPPER(II)-N-THIOCYANATE COMPLEXES WITH ANILINE AND SOME OF ITS DERIVATIVES

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We have obtained and characterized by IR, electronic and EPR spectroscopy the $Cu(NCS)_2L_2$ group of complexes ($L = C_6H_5NH_2$, o-$CH_3C_6H_4NH_2$, m-$CH_3C_6H_4NH_2$, p-$CH_3C_6H_4NH_2$ m-$NO_2C_6H_4NH_2$, p-NO_2(o-CH_3)$C_6H_3NH_2$ and p-$ClC_6H_4NH_2$). From the IR spectra it is inferred that in all complexes, coordination of the thiocyanate groups to the metal takes place through the nitrogen atoms, these being placed in terminal and *trans* positions. The electronic spectra in ethanol solution indicate pseudo-octahedral geometry with tetragonal distortion and with axial interaction by molecules of the solvent. From the EPR spectra in the solid and in ethanol solution it is inferred that all the complexes are monomeric.

INTRODUCTION

Complexes such as $Cu(NCS)_2L_2$, where L represents pyridine derivatives, have already been studied[1,2] and it has been observed that the ligands with substituents in α positions can provoke steric hindrance and can influence the way of coordinating the thiocyanate group.

We have selected in our work aniline and some of its derivatives as ligands. These are weaker Lewis bases than the pyridine derivatives, basically due to the less effective charge around the nitrogen ($-0.59\ e^-$ in pyridine and $+0.09\ e^-$ in aniline); then the steric hindrance which the benzene ring substituents provoke, will therefore be weaker. In order to carry out a comparative study we have used ligands with substituents in α position and also others in 3 and 4 positions. Furthermore, we have used aniline derivatives with either donor substituents (o-$CH_3C_6H_4NH_2$, m-$CH_3C_6H_4NH_2$, p-$CH_3C_6H_4NH_2$) or acceptor substituents (p-$ClC_6H_4NH_2$, m-$NO_2C_6H_4NH_2$, p-$NO_2$$o$-$CH_3C_6H_3NH_2$), in order to compare with the aniline and observe the influence of the substituents in the different vibration modes.

EXPERIMENTAL

All reactions were carried out in a similar way as follows: 2.00 g (8 mmol) of $CuSO_4 \cdot 5H_2O$ are dissolved in 100 cm^3 of distilled water. To this solution ethanol solutions of the different ligands are added with stirring in every case. The ratio of the Cu(II) and that of the Lewis base must be 1:2. Subsequently, a solution of 1.23 g (16 mmol) of NH_4NCS in 150 cm^3 of distilled water is added in every case.

Immediately, different brown or green solids appear, which are filtered off, washed several times with ethanol and dried in vacuum. Yield: 98%.

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RESULTS

Anal. Calcd. for $Cu(NCS)_2(C_6H_5NH_2)_2$:Cu, 17.38; N, 15.31; C, 45.95; H, 3.82. Found: Cu, 17.23; N, 15.86; C, 45.48; H, 3.15.

Calcd. for $Cu(NCS)_2(o\text{-}CH_3C_6H_4NH_2)_2$:Cu, 16.14; N, 14.22; C, 48.78; H, 4.57. Found:Cu, 16.05; N, 14.14; C, 47.98; H, 4.52.

Calcd. for $Cu(NCS)_2(m\text{-}CH_3C_6H_4NH_2)_2$:Cu, 16.14; N, 14.22; C, 48.78; H, 4.57. Found:Cu, 15.98; N, 14.13; C, 48.52; H, 4.82.

Calcd. for $Cu(NCS)_2(p\text{-}CH_3C_6H_4NH_2)_2$:Cu, 16.14; N, 14.22; C, 48.78; H, 4.57. Found:Cu, 16.22; N, 14.20; C, 48.34; H, 4.64.

Calcd. for $Cu(NCS)_2(p\text{-}ClC_6H_4NH_2)_2$: Cu, 14.62; N, 12.89; C, 38.67; H, 2.76; Cl, 16.31. Found: Cu, 14.48; N, 12.85; C, 38.77; H, 2.95, Cl, 16.10.

Calcd. for $Cu(NCS)_2(m\text{-}NO_2C_6H_4NH_2)_2$: Cu, 13.94; N, 18.44; C, 36.88; H, 2.63. Found: Cu, 13.82; N, 18.35; C, 36.24; H, 2.54.

Calcd. for $Cu(NCS)_2(p\text{-}NO_2o\text{-}CH_3C_6H_3NH_2)_2$: Cu, 13.14; N, 17.37; C, 39.70; H, 3.30. Found: Cu, 13.26; N, 17.34; C, 40.03; H. 3.23.

The Cu was determined by titration of the Cu-EDTA complex in presence of murexide as indicator. The Cl^- was determined by the Volhard method.

The IR spectra were recorded on a Beckman 20A spectrophotometer in the range 4000–250 cm^{-1}, using Nujol and CsI windows.

The electronic spectra were recorded on a Pye Unicam SP8-100 spectrophotometer in the 11,1-28,0 kK range in solutions of ethanol.

The EPR spectra was recorded on a Varian E-12 at a microwave frequency of 9 GHz (X-band) using DPPH for calibration. At low temperature, the spectra were recorded in a variable temperature cell.

DISCUSSION

IR spectra

The addition of ethanol solutions of aniline and some of its derivatives to aqueous solutions of $CuSO_4 \cdot 5H_2O$ in a ratio of 2:1, in the presence of NH_4NCS, causes the precipitation of green or brown coloured solids, with stoichiometry $Cu(NCS)_2L_2$ (L = aniline and its deriva-

TABLE I
Vibrational frequencies (cm^{-1}, IR) of the amine groups in the $Cu(NCS)_2L_2$ complexes

$Cu(NCS)_2L_2$	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\delta(NH_2)$
L = $C_6H_5NH_2$	3308s	3218s	1615s 1592s
$o\text{-}CH_3C_6H_4NH_2$	3302s	3228s	1625m 1600m 1586s
$m\text{-}CH_3C_6H_4NH_2$	3300s	3220s	1628m 1610s 1595s
$p\text{-}CH_3C_6H_4NH_2$	3300s	3225s	1628w 1590s
$m\text{-}NO_2C_6H_4NH_2$		3220w	1598w
$p\text{-}ClC_6H_4NH_2$	3300s	3218s	1608m 1588s
$p\text{-}NO_2o\text{-}CH_3C_6H_3NH_2$	3320m	3250m	1595s

s = strong; m = medium; w = weak.

TABLE II
Vibrational frequencies (cm^{-1}, IR) of the NCS groups in the $Cu(NCS)_2L_2$ complexes

$Cu(NCS)_2L_2$	ν_{as}(NCS)	ν_s(NCS)	δ(NCS)	ν(Cu-NCS)
L = $C_6H_5NH_2$	2120vs	823m	478w	325m, b
o-$CH_3C_6H_4NH_2$	2110vs	838m	475w	348sh, w
m-$CH_3C_6H_4NH_2$	2120vs	828w	465vw	320m, b
p-$CH_3C_6H_4NH_2$	2122vs	842w	478w	325m, b
m-$NO_2C_6H_4NH_2$	2100s	840w	475w	320w, b
p-$ClC_6H_4NH_2$	2115vs	825s	475w	320m, b
p-NO_2o-$CH_3C_6H_3NH_2$	2110vs	842vs	480w	330s, b

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; b = broad; sh = shoulder.

tives). We have recorded the IR spectra of the complexes in the range 4000–250 cm^{-1} and the spectroscopic results are reported in Tables I and II. The bands of the amine groups appear in a similar range to other coordination compounds.[3,4] In relation to a thiocyanate group, the ν_2(NCS) is the most characteristic one in order to propose the coordination mode. It is observed in the range 842–823 cm^{-1}, which means that the bond is through the nitrogen.[5–9]

In all the complexes studied there is a possibility for *cis-trans* isomerism. As we have observed only one band ν_{as}(NCS) and also one for ν_s(NCS) in the IR spectra of all the compounds, we propose for all the molecules one centrosymmetric structure (*trans*). This structure is similar to that of other Cu(II) cyanate complexes already described in the literature.[10,11] As a final comment it is necessary to mention that in all the complexes only one band for the (Cu-NCS) stretching vibration is observed, which is in agreement with the *trans* structure we have already proposed.

Electronic spectra

These were obtained in ethanol solution and are reported in Table III. In all complexes a broad band is observed with an absorption maximum in the 12.5–13.5 kK range, which can be assigned to the $(^2E_g, {}^2B_{2g}) \leftarrow {}^2B_{1g}$ transition and a very intense band in the range 25.0–26.4 kK, which corresponds to the electronic charge-transfer SCN → Cu(II). These spectra are characteristic of a pseudooctahedral geometry with tetragonal distortion[12–14] with an interaction in the two axial positions of solvent molecules.[4]

In these complexes, in which the Cu^{2+} ion is coordinated to 4 nitrogen atoms (almost

TABLE III
Electronic spectra of the $Cu(NCS)_2L_2$ complexes

$Cu(NCS)_2L_2$	$\tilde{\nu}_{max}$[a] (in kK)
L = $C_6H_5NH_2$	12,7; 25,1
o-$CH_3C_6H_4NH_2$	13,0; 25,1
m-$CH_3C_6H_4NH_2$	13,1; 25,0
p-$CH_3C_6H_4NH_2$	13,5; 25,3
m-$NO_2C_6H_4NH_2$	12,5; 26,0
p-$ClC_6H_4NH_2$	12,7; 25,2
p-NO_2o-$CH_3C_6H_3NH_2$	12,5; 26,4

[a]In ethanol solution.

equivalent as inferred by the EPR spectra), the two thiocyanate groups and the two L ligands occupy *trans* positions. It is logical that the field created by the nitrogen atoms of N-coordinated NCS is stronger than that of the sulphur atoms. Looking at the $\bar{\nu}_{max}$(kK) values obtained for the $Cu(NCS)_2L_2$ complexes, where there are no important differences between the complexes with L ligands with substituents in α position and those without this type of substituent, it is possible to see that the former do not present any steric hindrance which provokes a bigger tetragonal distortion.

EPR spectra

Figure 1 represents the EPR spectra of the crystalline powder of some of the synthesized complexes. All the complexes present anisotropic spectra, and for all them, g_0 is in the range of 2100–2120 (Table IV), which is in agreement with a non-degenerate fundamental state.[15]

As observed in Figure 1, two different types of spectra are obtained. The spectra of the complexes with *p*-$CH_3C_6H_4NH_2$, *m*-$NO_2C_6H_4NH_2$ and *p*-NO_2-*o*-$CH_3C_6H_3NH_2$ present three

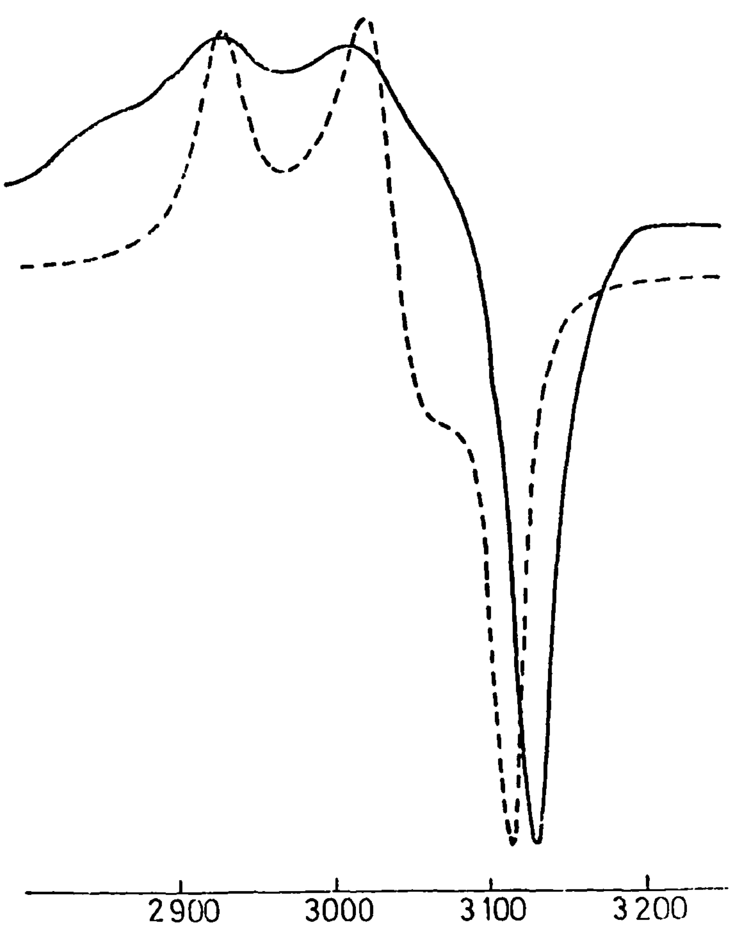

FIGURE 1 X-Band spectra of powder — $Cu(NCS)_2$(*o*-$CH_3C_6H_4NH_2$)$_2$ .... $Cu(NCS)_2$(*p*-$CH_3C_6H_4NH_2$)$_2$

TABLE IV
Powder g values for the $Cu(NCS)_2L_2$ complexes

$Cu(NCS)_2L_2$	g_1	g_2	g_3	g_0
L = $C_6H_5NH_2$	2.061	2.096	2.186	2.114
o-$CH_3C_6H_4NH_2$	2.063	2.090	2.187	2.113
m-$CH_3C_6H_4NH_2$	2.070	2.090	2.188	2.116
p-$CH_3C_6H_4NH_2$	2.057	2.070	2.192	2.106
m-$NO_2C_6H_4NH_2$	2.046	2.066	2.198	2.103
p-$ClC_6H_4NH_2$	2.066	2.106	2.191	2.121
p-NO_2o-$CH_3C_6H_3NH_2$	2.056	2.070	2.238	2.121

g values, but one of them is very poorly resolved. The small anisotropy observed could be due to the existence of a weak rhombic component probably arising from distortions in the xy plane.

The complexes with $C_6H_5NH_2$, p-$ClC_6H_4NH_2$ and o-$CH_3C_6H_4NH_2$ and m-$CH_3C_6C_4NH_2$ give rise to typical orthorhombic spectra with three g values similar to those described in the literature.[15,16] The existence of orthorhombic symmetry is probably due to the presence of two complex crystallographically non-equivalent molecules.[16]

The EPR spectra in ethanol at room temperature are very broad and not well resolved, from which it was not possible to obtain any of the g_{iso} and A_{iso} parameters. However in frozen solutions (−160°C), all complexes present very well resolved spectra which indicate monomeric species (Figure 2). The parallel component of the hyperfine splitting of the copper appears well resolved with a relatively high $A_{\parallel}$ (Cu) (Table V). This split is not

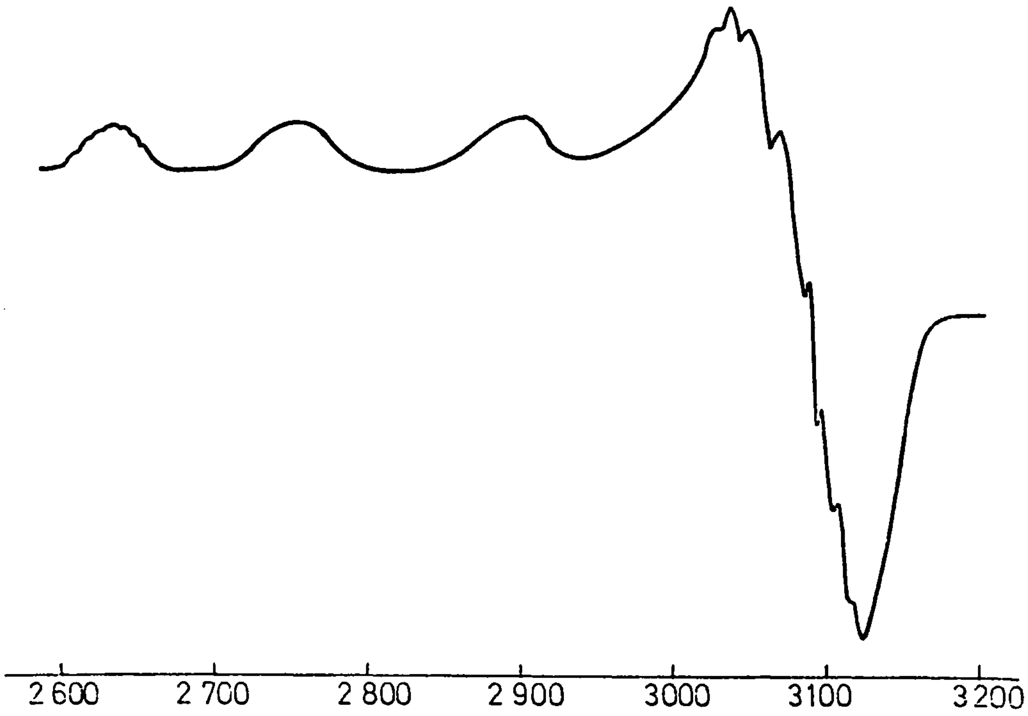

FIGURE 2 X-Band EPR spectra of $Cu(NCS)_2L_2$ complexes at −160°C.

TABLE V
EPR parameters and bonding parameter for the $Cu(NCS)_2L_2$ complexes in ethanol solution

$Cu(NCS)_2L_2$	$g_\parallel$	$g_\perp$	$A_\parallel^{Cu\,a}$	$A_\perp^{N\,a}$	$A_\parallel^{N\,a}$	α^2	α'^2	β_1^2	β^2
L = $C_6H_5NH_2$	2.301	2.079	167.5	14.5	16.1	0.83	0.26	0.69	0.73
o-$CH_3C_6H_4NH_2$	2.298	2.066	163.0	12.5	13.8	0.76	0.28	0.77	0.62
m-$CH_3C_6H_4NH_2$	2.312	2.078	161.9	16.0	17.7	0.83	0.26	0.74	0.74
p-$CH_3C_6H_4NH_2$	2.294	2.077	176.7	14.5	16.06	0.85	0.44	0.70	0.74
m-$NO_2C_6H_4NH_2$	2.262	2.090	151.0	14.0	15.0	0.74	0.36	0.70	0.71
p-$ClC_6H_4NH_2$	2.295	2.078	160.7	14.5	16.0	0.81	0.28	0.69	0.73
p-NO_2o-$CH_3C_6H_3NH_2$	2.265	2.091	153.3	12.7	13.70	0.76	0.32	0.66	0.78

[a] In 10^{-4} cm^{-1}.

observed in the perpendicular components because the $A_\perp$ (Cu) must be very low.[17] In all cases, the hyperfine split of the ^{14}N atoms of the ligands, was obtained, in both parallel and perpendicular components, indicating that the four nitrogen atoms are almost equivalent.

These spectra, recorded at low temperature, can be interpreted using the Hamiltonian spin for axial symmetry:

$$\hat{H} = \beta_e[g_\parallel H_z\hat{S}_z + g_\perp (H_x\hat{S}_x + H_y\hat{S}_y) + A_\parallel \hat{S}_z\hat{I}_z + A_\perp (\hat{S}_x\hat{I}_x + \hat{S}_y\hat{I}_y) + \Sigma_N \hat{S}A^N\hat{I}^N]$$

The experimentally determined parameters for this Hamiltonian operator are reported in Table V. Assuming D_{4h} symmetry, the antibonding molecular orbitals are obtained by the equations described in the literature.[18–20] The calculated values for these parameters are also reported in Table V. The found values for α^2 and α'^2 indicate a deep delocalisation of the non paired electrons in the B_{1g}MO, and they are very similar to those found in other complexes of $Cu(NCO)_2L_2$.[17] The β_1^2 values indicate a significant covalency in the π bond both in and out of the plane, this result being similar to that found in other Cu complexes.[17,18]

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