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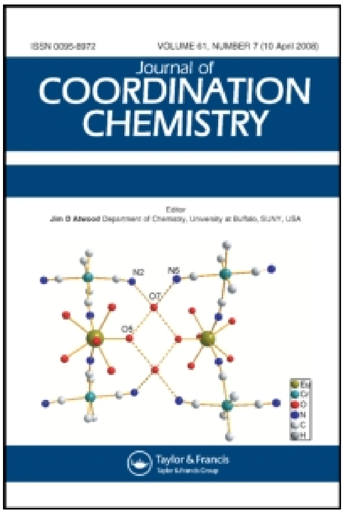

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Syntheses, structures, and spectroscopic properties of copper(II) and cobalt(III) complexes containing 1,4,7-tribenzyl-1,4,7-triazacyclononane ligand

Yong-Sheng Yang[a]; Wen Gu[a]; Jing Qian[a]; Feng-Xian Gao[a]; Shi-Ping Yan[a]
[a] Department of chemistry, Nankai University 300071, Tianjin, People's Republic of China

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Syntheses, structures, and spectroscopic properties of copper(II) and cobalt(III) complexes containing 1,4,7-tribenzyl-1,4,7-triazacyclononane ligand

YONG-SHENG YANG, WEN GU, JING QIAN, FENG-XIAN GAO
and SHI-PING YAN*

Department of chemistry, Nankai University 300071, Tianjin,
People's Republic of China

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Three new complexes $[CuL(N_3)_2]$ (**1**), $[CuL(SCN)_2]$ (**2**), and $[CoL(SCN)_3]$ (**3**) ($L = 1,4,7$-tribenzyl-1,4,7-triazacyclononane) have been synthesized and structurally characterized. Complex **1** crystallizes in monoclinic space group $P2(1)/n$ with unit cell parameters $a = 14.105(7)$, $b = 8.999(5)$, $c = 21.603(11)$ Å, $\beta = 100.470(7)°$. While **2** crystallizes in triclinic space group P-1 with unit cell parameters $a = 9.6380(16)$, $b = 10.6993(18)$, $c = 15.798(3)$ Å, $\alpha = 106.636(3)$, $\gamma = 116.478(3)°$. Complex **3** crystallizes in trigonal space group P–$3c1$ with unit cell parameters $a = 14.744(3)$, $b = 14.744(3)$, $c = 16.098(4)$ Å, $\gamma = 120°$. Elemental analysis, IR, UV-vis spectra of complexes **1**–**3** and ESR spectra of complexes **1**–**2** were also determined.

Keywords: Copper; Cobalt; Macrocyclic ligands; Crystal structure; Spectroscopic properties

1. Introduction

1,4,7-Triazacyclononane (tacn) and its derivatives are included in a wide range of metal-organic compounds due to the coordination preference for transition metal ions. The past three decades have witnessed a rapid development coordination chemistry of tacn [1]; tacn and its N-substituted complexes are excellent ligands in supporting both mono- and bi-metallic complexes containing liable coordination sites. Hence, many tacn and its N-substituted complexes are both structural and functional models of various metalloenzymes [2–8], capable of promoting phosphate ester degradation with DNA [9–13] or RNA [14, 15] cleavage and used in oxidative catalysis [16]. Previously, much of this work focused on Cu(II)-and-L-containing complexes, but the analogous Co(III) complexes have received much less attention. In this paper, three complexes containing copper and cobalt ions with the ligand L: $[CuL(N_3)_2]$ (**1**), $[CuL(SCN)_2]$ (**2**), and $[CoL(SCN)_3]$ (**3**) have been prepared and characterized by

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*Corresponding author. Email: yansp@mail.nankai.edu.cn

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single-crystal X-ray diffraction and spectroscopic properties. We previously reported similar compounds with another N-substituted ligand 1,4,7-triisopropyl-1,4,7-triazacyclononane [17].

2. Experimental

2.1. *Materials and instrumentation*

1,4,7-Triazacyclononane (tacn) was prepared according to the previous procedure [18, 19] and the 1,4,7-tribenzyl-1,4,7-triazacyclononane was prepared according to the literature [20]. All starting materials and solvents were of analytical purity.

Elemental analyses for C, H and N were carried out on a Model 240 Perkin-Elmer instrument. IR spectra were measured using KBr disks in a Bruker Tensor 27 FTIR spectrophotometer in the 400–4000 cm^{-1} region. The UV-vis spectra were measured on a Jasci V-570 UV-vis spectrophotometer in the 200–2000 nm region. The ESR spectra were measured on a ER 200D-SRC spectrophotometer in the X-bond scan.

2.2. *Preparation of compounds*

$[CuL(N_3)_2]$ (1): A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ 0.1850 g (0.5 mmol) in acetonitrile (10 ml) was added to a solution of L 0.040 g (0.5 mmol) in acetonitrile (5 ml). The reaction mixture was stirred at room temperature and gave a turbid solution and 30 min later afforded a clear deep-blue solution. Then a solution of NaN_3 0.065 g (1 mmol) in water (5 ml) was slowly added. The reaction mixture was continuously stirred for 2 h and filtered to get rid of insoluble particles. Deep blue crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of the filtrate. Anal. Calcd for **1** (%): C, 59.27; H, 6.08; N, 23.04. Found: C, 59.52; H, 6.25; N, 22.96.

$[CuL(SCN)_2]$ (2): Complex **2** was synthesized with a similar method to **1**. A suspension of $Cu(ClO_4)_2 \cdot 6H_2O$ 0.1850 g (0.5 mmol) and the ligand L 0.040 g (0.5 mmol) in acetonitrile (20 mL) give a blue solution; NH_4SCN 0.076 g (1 mmol) in water (5 mL) was added slowly to the solution and the deep blue precipitate was generated, filtered off, washed with ethanol and ether, and dried under vacuum (45% yield). Crystals suitable for X-ray crystallographic analysis of **2** were obtained by recrystallizing from DMF and slowly evaporating the filtrate. Anal. Calcd for **2** (%): C, 60.18; H, 5.78; N, 12.04. Found: C, 60.13; H, 5.70; N, 12.09.

$[CoL(SCN)_3]$ (3): Complex **3** was prepared in an analogous manner to that of **2** but using $Co(ClO_4)_2 \cdot 6H_2O$ instead of $Cu(ClO_4)_2 \cdot 6H_2O$. The precipitate was recrystallized in the mixed solvent of DMF/CH_3CN (1 : 1) to afford crystals suitable for X-ray crystallographic analysis. Anal. Calcd for **3** (%): C, 57.02; H, 5.18; N, 13.24. Found: C, 56.95; H, 5.22; N, 13.28.

Caution: Although no problems were encountered in this work, perchlorate complexes containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.

2.3. *X-ray crystallography*

Diffraction data for **1** and **2** were collected at 293 K, and **3** at 294 K, with a Bruker SMART 1000 CCD diffractometer using Mo–Kα radiation ($\lambda = 0.71073$ Å) with the ω–2θ scan technique. An empirical absorption correction (SADABS) was applied to raw intensities [21]. The structures were solved by direct methods (SHELX-97) and refined by full-matrix least-squares procedures on F^2 using SHELX-97 [22]. The hydrogen atoms were added theoretically, and riding on the concerned atoms and refined with fixed thermal factors. Further details about crystal data and structure refinement are summarized in table 1. The reference CCDC: 608849(**1**); 614285(**2**) and 610110(**3**).

3. Results and discussion

The structures of complexes **1**–**3** are shown in figures 1–3, respectively, and their selected bond lengths and angles are listed in table 2. In complexes **1** and **2**, the Cu ions are five- coordinate, three N atoms from ligand L and two N atoms from N_3^-/or SCN^- ligands. For the purpose of discussion, we chose complex **1** to describe. In figure 1, the basal plane is occupied by N(1) and N(3) from the L ligand and N(4) and N(7) from azide, with average Cu–N_L and Cu–N_{azide} bond lengths of 2.111 and 1.983 Å, respectively, which are comparable with that of $[CuL'(N_3)_2]$ (2.155 and 1.994 Å) (L′ = 1,4,7-triisopropyl-1,4,7-triazacyclononane) [17] and $[Cu\ L''(N_3)_2]$ (2.060 and 2.009 Å) (L″ = 1,4,7-trimethyl-1,4,7-triazacyclononane) [23]. The apical position is occupied by N(2) from L with a longer bond distance (2.2490 Å) than those in the basal plane, almost the same as that of $[CuL'(N_3)_2]$ (2.260 Å) [17] and slightly shorter than that of $[Cu\ L''(N_3)_2]$ (2.290 Å) [23]. The Cu atom is displaced out of the basal plane by 0.105 Å in the direction of the axial atom, which is normally observed for five-coordinate square pyramidal geometry. The value of τ defined by Addison *et al.* [24] is 0.133 [$\tau = (\beta - \alpha)/60$, where $\alpha = $ N(4)–Cu(1)–N(3) $= 168.40(8)$, $\beta = $ N(7)–Cu(1)–N(1) $= 176.47(7)^\circ$, $\tau = 0$ and 1 for perfect square-pyramidal and trigonal-bipyramidal geometries, respectively] indicating the occurrence of a slight distortion for this square-pyramidal geometry. The τ values in the structurally characterized $[CuL]^+$ or $[CuL]^{2+}$ with different terminal ligands, are listed in table 3. In complex **2**, the average Cu–N_L and Cu–N_{SCN^-} bond lengths in the basal plane are 2.083(3) and 1.976(4) Å, respectively, and the axial bond is also relatively longer [2.240(4) Å]. The corresponding τ value is 0.0935, which suggests a more systematic regularity in the geometry than that found in complex **1**. The difference τ values for **1** and **2** indicates that a more regular conformation is observed when the auxiliary ligand changes from azide to thiocyanate, as also occurred in $[CuL'(N_3)_2]$ and $[CuL'(SCN)_2]$ [17].

Table 1. Data collection and processing parameters for complexes **1**, **2** and **3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{27}H_{33}CuN_9$	$C_{29}H_{33}CuN_5S_2$	$C_{30}H_{33}CoN_6S_3$
Formula weight	547.16	579.26	632.73
Temperature (K)	293(2)	293(2)	294(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, *P*2(1)/*n*	Triclinic, *P*-1	Trigonal, *P*-3*c*1
Unit cell dimensions (Å °)			
a	14.105(7)	9.6380(16)	14.744(3)
b	8.999(5)	10.6993(18)	14.744(3)
c	21.603(11)	15.798(3)	16.098(4)
α	90	106.636(3)	90
β	100.470(7)	100.47	90
γ	90	116.478(3)	120
Volume (Å^{-3})	2696(2)	1381.5(4)	3030.6(11)
Z, Calculated density (Mg m^{-3})	4, 1.348	2, 1.393	4, 1.387
Absorption coefficient (mm^{-1})	0.844	0.969	0.804
F(000)	1148	606	1320
Crystal size (mm)	0.28 × 0.22 × 0.20	0.20 × 0.18 × 0.14	0.24 × 0.20 × 0.12
θ range for data collection (°)	1.89 to 25.03	1.36 to 25.02	1.59 to 25.02
Limiting indices	$-16 \le h \le 7$, $-10 \le k \le 10$, $-25 \le l \le 25$	$-1 \le h \le 6$, $-12 \le k \le 12$, $-18 \le l \le 18$	$-17 \le h \le 17$, $-17 \le k \le 17$, $-19 \le l \le 18$
Reflections collected/unique	14088/4753	7077/4853	14375/1788
R(int)	0.0226	0.0356	0.1350
Max. and min. transmission	1.000000 and 0.696295	1.000000 and 0.576189	1.000000 and 0.610173
Data/restraints/parameters	4753/0/334	4853/0/334	1788/18/109
Goodness-of-fit on F^2	1.024	1.000	1.150
Final *R* indices [$\dot{I} > 2\theta(\dot{I})$]	$R_1 = 0.0285$, $wR_2 = 0.0746$	$R_1 = 0.0490$, $wR_2 = 0.1009$	$R_1 = 0.0574$, $wR_2 = 0.1187$
R indices (all data)	$R_1 = 0.0391$, $wR_2 = 0.0792$	$R_1 = 0.1001$, $wR_2 = 0.1277$	$R_1 = 0.1696$, $wR_2 = 0.1870$
Largest diff. peak and hole(e Å^{-3})	0.372 and −0.232	0.441 and −0.446	0.543 and −0.473

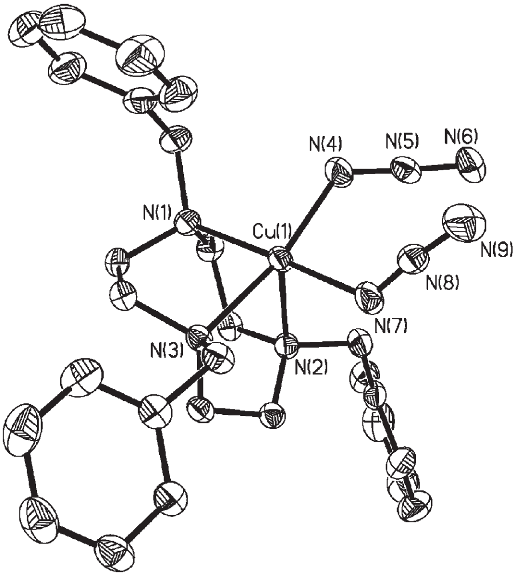


Figure 1. Perspective view of **1** with the atom-numbering scheme. Thermal ellipsoids represent 30% probability and hydrogen atoms are omitted for clarity.

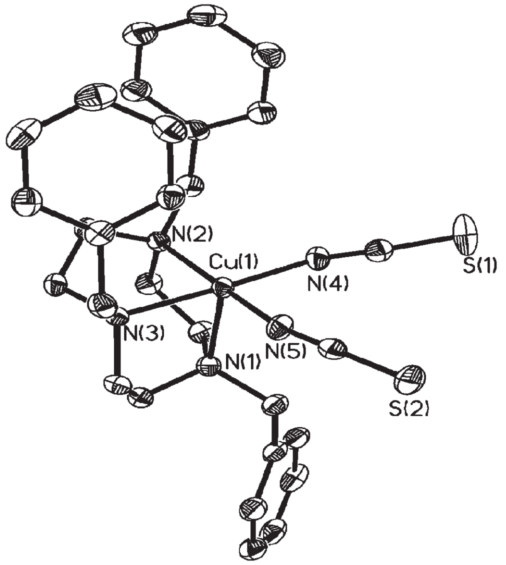


Figure 2. Perspective view of complex **2** with the atom-numbering scheme. Thermal ellipsoids represent 30% probability; hydrogen atoms are omitted for clarity.

In complex **3**, the Co(III) ion is coordinated by six N atoms from the ligand L and thiocyanates and formed a distorted octahedral coordination geometry. The bond lengths of Co–N_L and Co–N_{SCN^-} are 1.984(6) and 1.903(7) Å, respectively. The bond angles N(1A)–Co(1)–N(1B), N(1A)–Co(1)–N(1), N(1)–Co(1)–N(1B) and

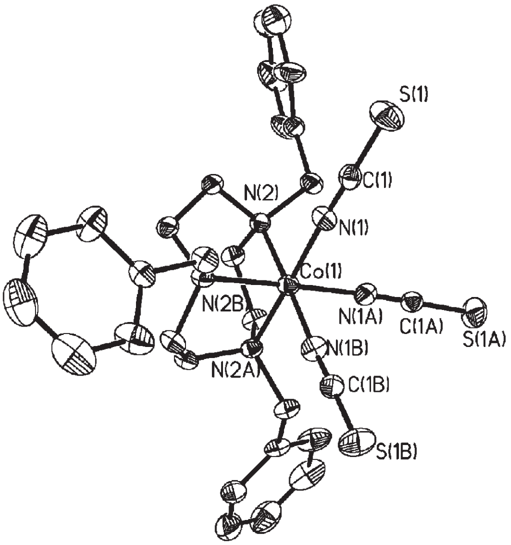


Figure 3. Perspective view of **3** with the atom-numbering scheme. Thermal ellipsoids represent 30% probability; hydrogen atoms are omitted for clarity.

N(2A)–Co(1)–N(2B), N(2A)–Co(1)–N(2), N(2)–Co(1)–N(2B) are the same, respectively [89.6(3) and 87.2(2)°]. The plane of three phenyls is located in the same side of the plane of tacn (N2, N2A, N2B) for better coordination to Co(III). The angle of thiocyanate(S–C–N) is almost linear (178.95°).

4. IR spectrum

All of the complexes have similar IR spectra. The $\nu_{(C\text{–}H)}$ stretching frequency of L is indicated by a shoulder involving a split sharp peak at 2934 cm^{-1}. A strong absorption, $\nu_{asym}(N_3)$, at 2053 cm^{-1} is observed for complex **1**, however, the weak absorption band at about 1300 cm^{-1} [$\nu_{sym}(N_3)$] could not be identified unambiguously due to overlapping bands in this region of the coordinated macrocycle. In the complex which contains N_3^-, terminal coordinated N_3^- and μ-1,3 -azide bridging ligands show similar absorptions [23]. The band at 2053 cm^{-1} shows that the azide is a terminal ligand rather than μ-1,3 bridging ligand ($\nu_{asym}(N_3)$ at 2100 cm^{-1}). This result was consistent with the crystal structure. In complexes **2** and **3**, the presence of NCS^- stretching vibrations at 2054 and 2055 cm^{-1} suggest that this group is coordinated to the metal ions as a terminal ligand. The band at 2100 cm^{-1} falls in the region expected for an end-to-end bridging ligand and that at 2050 cm^{-1} in the region expected for terminal NCS^- [25, 26]. These data can be also confirmed in similar compounds with L′ [17]. Additionally, abundant absorption peaks in the region 670–840 cm^{-1} strongly argue for the presence of phenyls. All of these results are consistent with the crystal structure.

Table 2. Selected bond lengths (A) and angles (°) for **1**, **2** and **3**.

1			
Cu(1)–N(4)	1.9810(19)	N(4)–N(5)	1.189(3)
Cu(1)–N(7)	1.9844(19)	N(5)–N(6)	1.156(2)
Cu(1)–N(2)	2.2490(18)	N(7)–N(8)	1.149(3)
Cu(1)–N(1)	2.1045(17)	N(8)–N(9)	1.164(3)
Cu(1)–N(3)	2.1165(16)		
N(4)–Cu(1)–N(7)	93.18(9)	N(4)–Cu(1)–N(7)93.18(9)	89.63(8)
N(7)–Cu(1)–N(1)	176.47(7)	N(4)–Cu(1)–N(3)	168.40(8)
N(7)–Cu(1)–N(3)	92.75(7)	N(1)–Cu(1)–N(3)	84.11(7)
N(4)–Cu(1)–N(2)	106.05(8)	N(7)–Cu(1)–N(2)	97.56(8)
N(1)–Cu(1)–N(2)	83.69(6)	N(3)–Cu(1)–N(2)	83.02(6)
N(5)–N(4)–Cu(1)	123.99(15)	N(6)–N(5)–N(4)	177.0(2)
N(8)–N(7)–Cu(1)	125.46(16)	N(7)–N(8)–N(9)	174.6(2)
2			
Cu(1)–N(5)	1.974(4)	Cu(1)–N(3)	2.079(3)
Cu(1)–N(4)	1.978(4)	Cu(1)–N(2)	2.087(4)
Cu(1)–N(1)	2.240(4)		
N(5)–Cu(1)–N(4)	89.98(17)	N(5)–Cu(1)–N(3)	92.09(15)
N(4)–Cu(1)–N(3)	177.65(17)	N(5)–Cu(1)–N(2)	172.04(16)
N(4)–Cu(1)–N(2)	94.21(15)	N(3)–Cu(1)–N(2)	83.60(14)
N(5)–Cu(1)–N(1)	100.83(15)	N(4)–Cu(1)–N(1)	97.24(16)
N(3)–Cu(1)–N(1)	83.46(14)	N(2)–Cu(1)–N(1)	85.37(14)
C(1)–N(1)–Cu(1)	109.9(3)	C(10)–N(2)–Cu(1)	117.6(3)
C(19)–N(3)–Cu(1)	114.0(3)		
3			
Co(1)–N(1A)	1.903(7)	Co(1)–N(1A)	1.903(7)
Co(1)–N(1B)	1.903(7)	Co(1)–N(2)	1.984(6)
Co(1)–N(2A)	1.984(6)	Co(1)–N(2B)	1.984(6)
N(1A)–Co(1)–N(1)	89.6(3)	N(1A)–Co(1)–N(1B)	89.6(3)
N(1)–Co(1)–N(1B)	89.6(3)	N(1A)–Co(1)–N(2)	92.5(2)
N(1)–Co(1)–N(2)	90.6(3)	N(1B)–Co(1)–N(2)	177.8(3)
N(1A)–Co(1)–N(2A)	90.6(3)	N(1A)–Co(1)–N(2A)	177.8(3)
N(1B)–Co(1)–N(2A)	92.5(3)	N(2)–Co(1)–N(2A)	87.2(2)
N(1A)–Co(1)–N(2B)	177.8(3)	N(1A)–Co(1)–N(2B)	92.5(3)
N(1B)–Co(1)–N(2B)	90.6(3)	N(2)–Co(1)–N(2B)	87.2(2)
N(2A)–Co(1)–N(2B)	87.2(2)		

Table 3. Cu–N and Cu–O distance/Å and τ values for $[CuL]^+$ and $[CuL]^{2+}$ complexes.

Compound	Coord. sphere	Axial	Equatorial	τ	Ref.
1	5N	2.249	2.105, 2.117 1.984, 1.981	0.133	this work
2	5N	2.241	2.078, 2.088 1.974, 1.978	0.0935	this work
$[CuL(Cl_4cat)]$	3N, 2O	2.203	1.988, 2.001 2.024, 2.028	0.0255	[28]
$[CuL(fla)]^+$	3N, 2O	2.231	2.027, 2.040 1.917, 2.012	0.123	[29]
$[CuL(o\text{-bs})]^+$	3N, 2O	2.182	2.010, 2.001 2.068, 1.977	0.161	[29]

cat = tetrachloro-1,2-benzenediol; fla = flavonolate; *o*-bs = *o*-benzoylsalicylato.

5. Electronic spectrum

The electronic spectra of complexes **1** and **2** are similar (figure 4, table 4), showing very strong absorption bands at 263 nm for **1** and 298 nm for **2**, which can be attributed to π–π^* charger transfer of the ligand. The shoulder at 399 nm of complex **1** can be ascribed as $Cu^{II} \rightarrow L$ MLCT. In addition, a weak, broad absorption centered at 644 nm for **1** and 685 nm for **2** can be designated as the typical d–d electronic-transfer absorption in $Cu^{II}(3d^9)$ ground state in C_{4v}. In complex **3**, the spectrum comprising five bands at 261, 411, 562, 718 and 936 nm indicate typical absorptions for a octahedral coordinated, low spin Co^{III} complex [27]. The five absorption bands can be ascribed to the d–d electron-transfer bands in $Co^{III}(3d^6)$ ground state.

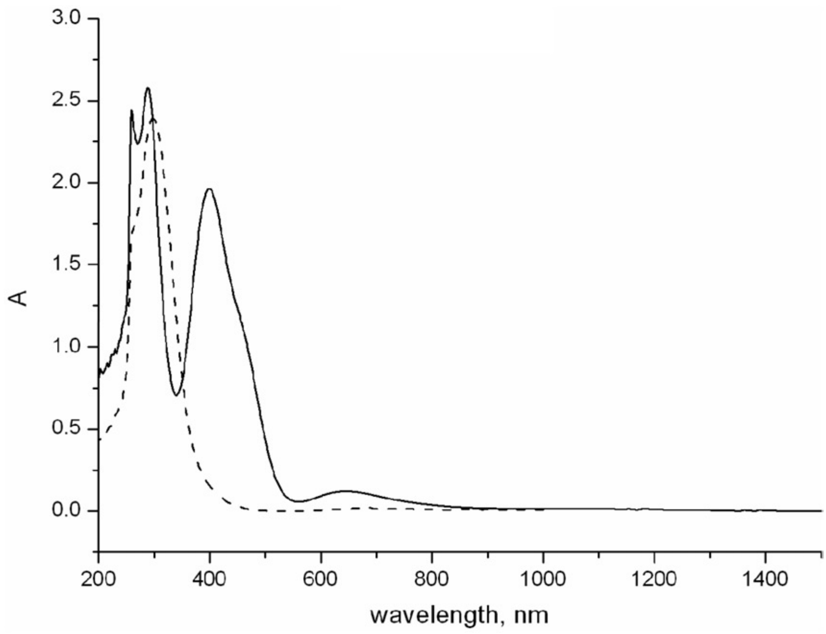
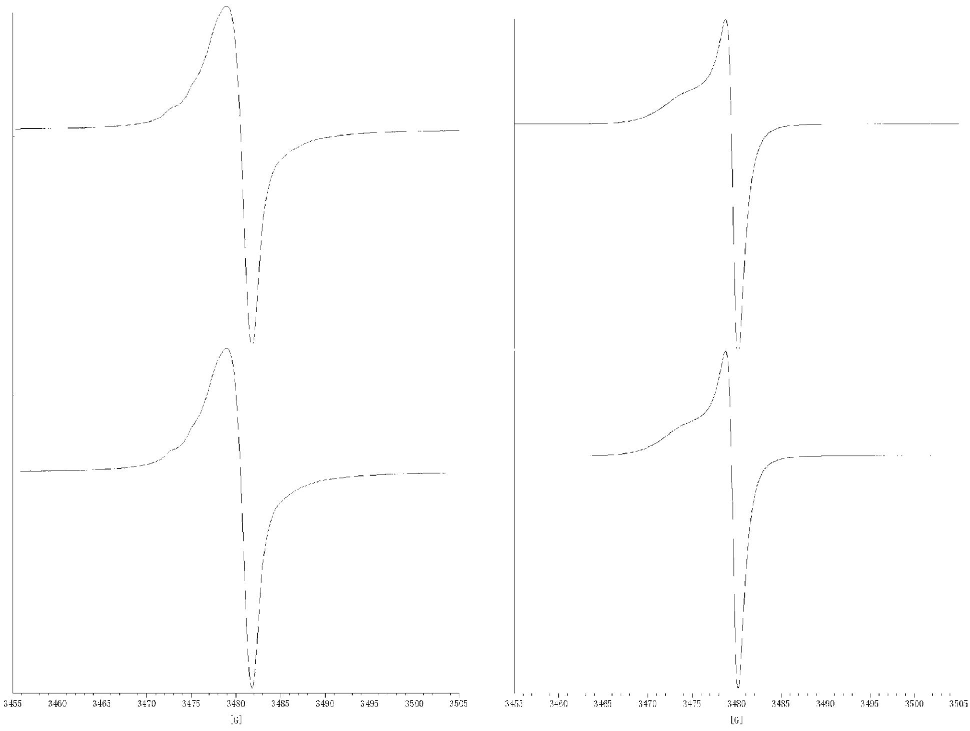


Figure 4. UV-vis spectra of DMSO solutions of $[CuL(N_3)_2]$ (—) and $[CuL(SCN)_2]$ (—).

Table 4. Summary of selected spectroscopic data for **1**, **2** and related complexes.

Complex	ESR	UV-vis λ_{max} (logε)	Ref.
1	$g_1 = 2.06$, $g_2 = 2.14$, $g_3 = 2.15$	288(2.23), 399(1.87), 644(1.69), 1021(1.38)	this work
2	$g_1 = 2.08$, $g_2 = 2.17$, $g_3 = 2.20$	298(3.25), 685(2.13), 841(1.87)	this work
$[CuL(Cl_4cat)]$	$g_1 = 2.24$, $g_2 = 2.05$, $g_3 = 2.01$,[a)]	265(4.11), 307(3.86), 485(1.70), 634(1.60), 990(1.30)[c)]	[28]
$[CuL(fla)]^+$	$g = 2.115$, $\mu_{eff} = 1.93$ BM.[b)]	269(4.23), 432(2.23), 615(2.90), 1040(1.73)[d)]	[29]
$[CuL(o\text{-bs})]^+$	$g = 2.120$, $\mu_{eff} = 1.99$ BM.[b)]	276(3.81), 650(1.96), 1035(1.62)[d)]	[29]

cat = tetrachloro-1,2-benzenediol; fla = flavonolate; *o*-bs = *o*-benzoylsalicylato a) measure at 77 K in CH2Cl2/Toluene. b) measured at room temperature in MeCN. c) measured at room temperature as solutions in CH_2Cl_2. d) measured at room temperature as solutions in DMF.



(a) (b)

Figure 5. X-band ESR spectra of complexes in powder at room temperature (top) and its computer simulation spectra (bottom). **1**(a), **2**(b).

6. ESR

The X-band ESR spectra of powdered complexes **1** and **2** at room temperature display an asymmetric absorption (figure 5). The computer simulation gave the ESR parameters $g_x = 2.06$, $g_y = 2.14$, $g_z = 2.15$ for **1** and $g_x = 2.08$, $g_y = 2.17$, $g_z = 2.20$ for **2**. The g values of **1** and **2** and related $[CuL]^+$ or $[CuL]^{2+}$ complexes are listed in table 4.

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