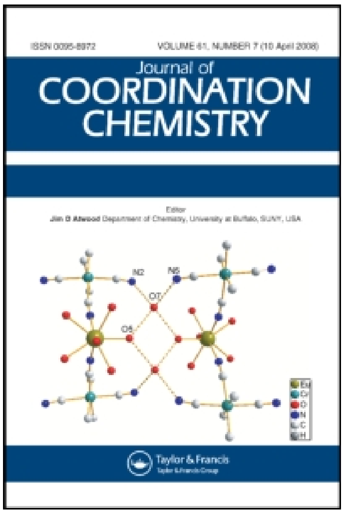

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Synthesis and crystal structure of new cobalt(II) and copper(II) complexes with deprotonated <i>N</i>-[2'-(4-methyl) pyrimidinyl]-2-nitrobenzenesulfonylurea

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Synthesis and crystal structure of new cobalt(II) and copper(II) complexes with deprotonated *N*-[2′-(4-methyl) pyrimidinyl]-2-nitrobenzenesulfonylurea

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Cobalt(II) and copper(II) complexes with deprotonated *N*-[2′-(4-methyl)pyrimidinyl]-2-nitrobenzenesulfonylurea were synthesized and their structures were characterized by IR spectrum, elemental analysis and X-ray diffraction. The deprotonated sulfonylurea is a bidentate ligand to Co(II) or Cu(II) in octahedral geometry. In the packing diagrams of the complexes, C–H $\cdots$ O hydrogen bonds are observed. The UV and fluorescence spectra of the complexes are described, and the thermogravimetric analyses of the complexes were performed.

Keywords: Cobalt(II); Copper(II); Sulfonylurea; Crystal structure

1. Introduction

Sulfonylurea compounds are herbicides with high efficiency and low toxicity. Their general structure is R_1–SO_2–NH–CO–NH–R_2, where R_1 can either be an aliphatic, aromatic, or heterocyclic group and R_2 can be a triazine or a pyrimidine ring. Sulfonylureas are widely used for controlling weeds in crops, such as rice, wheat, maize, barley, sugar beet, tomato, pigweed and leaf mustard [1–6]. In the environment, sulfonylurea herbicides can be easily decomposed owing to chemical and thermal instability. A variety of sulfonylurea compounds have been synthesized and some commercially developed [2–4]. The coordination chemistry of sulfonylurea drugs with transition-metal and d^{10} metals (such as the zinc(II), cadmium(II), mercury(II) and silver(I)) have been investigated [7, 8]. However, the coordination of the sulfonylurea containing pyrimidine ring is somewhat different from the

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complexes mentioned above. In order to obtain further information on the structural changes of different sulfonylurea complexes, we report here the synthesis and structural characterizations of cobalt(II) and copper(II) complexes $[Co(L^2)_2(DMSO)_2]$ (**3**) and $[Cu(L^2)_2(DMF)_2]$ (**4**) (L^2 = deprotonated *N*-[2′-(4-methyl)-pyrimidinyl]-2-nitrobenzenesulfonylurea, DMSO = dimethyl sulfoxide and DMF = dimethylformamide).

2. Experimental

2.1. *General methods*

Precursor ($\mathbf{L^1}$) was prepared according to literature methods [1, 2]. Melting points were determined with a Boetius Block apparatus. Elemental analyses were measured using a Perkin-Elmer 2400C elemental analyzer. IR spectra (KBr) were taken on a Bruker Equinox 55 spectrometer. UV spectra were carried out with a TU-1221 UV–VIS recording spectrophotometer. The luminescence spectra were conducted on a Cary Eclipse fluorescence spectrophotometer. The thermogravimetric analyses were carried out in nitrogen ($25\,cm^3\,min^{-1}$, 20–800°C, $10°C\,min^{-1}$) using a Netzsch STA 449C analyzer.

2.2. *Preparation of $[Co(L^2)_2(DMSO)_2]$ (3)*

$\mathbf{L^1}$ (0.2 g, 0.6 mmol) and NaOH (2.0 g, 0.05 mol) were dissolved in DMSO (5 mL) and water (20 mL) and stirred at room temperature for 10 min, then $Co(ClO_4)_2 \cdot 6H_2O$ (0.2 g, 0.6 mmol) was added and stirring continued at 40°C for 1 h. The filtrate of the above mixture was allowed to evaporate slowly under ambient conditions, and purple single crystals suitable for X-ray analysis were obtained within two weeks. Yield: 0.1 g (38%); m.p.: 230–232°C. Anal. Calc for $C_{28}H_{32}CoN_{10}O_{12}S_4$: C, 37.88; H, 3.63; N, 15.78%. Found: C, 37.49; H, 3.52; N, 15.83%. IR (KBr, cm^{-1}): 3368m, 3090m, 2933w, 2857w, 1668s, 1590s, 1379s, 1280s, 1179m. UV spectra absorption in CH_2Cl_2 (5.0×10^{-6} M) between 200 and 400 nm have adsorptions at 233 and 285 nm.

2.3. *Preparation of $[Cu(L^2)_2(DMF)_2]$ (4)*

$\mathbf{L^1}$ (0.2 g, 0.6 mmol) and NaOH (2.0 g, 0.05 mol) were dissolved in DMF (5 mL) and water (20 mL), stirred at room temperature for 10 min and then $CuCl_2$ (0.1 g, 0.6 mmol) was added continuing to stir at 40°C for 1 h. The filtrate of the above mixture was allowed to evaporate slowly under ambient conditions, and blue single crystals suitable for X-ray analysis were obtained within three weeks. Yield: 0.08 g (30%); m.p.: 188–190°C. Anal. Calc for $C_{30}H_{34}CuN_{12}O_{12}S_2$: C, 40.84; H, 3.88; N, 19.05%. Found: C, 40.64; H, 3.56; N, 19.43%. IR (KBr, cm^{-1}): 3374m, 3100m, 2942w, 2862w, 1660s, 1595s, 1386s, 1278s, 1199m. UV spectra absorption in

CH_2Cl_2 (5.0×10^{-6} M) between 200 and 400 nm show adsorptions at 240 and 276 nm.

2.4. *X-ray structure determination*

For **3** and **4**, selected single crystals were mounted on a Bruker APEX II CCD diffractometer at 293(2) K with Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω scan mode. Data collection and reduction were performed using the SMART and SAINT software [9] with frames of 0.6° oscillation in the θ range $1.8 < \theta < 25°$. An empirical absorption correction was applied using SADABS [10]. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package [11]. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and included in structure factor calculations. Selected bond lengths and angles are shown in table 1 and crystallographic data summarized in table 2 for **3** and **4**.

3. Results and discussion

3.1. *Preparation and crystal structure*

In **L**^{1} the hydrogen of N–H near the sulfamido group is more active than that adjacent to the pyrimidine ring due to electronic effects [3, 4] (scheme 1), and in solution this hydrogen reacts with sodium hydroxide to form an anion. As a result, delocalization between negative charge on the N atom and its neighboring C=O group occurs to

Table 1. Selected bond lengths (Å) and angles (deg) for **3** and **4**.

3		**4**	
Co(1)–O(1)	2.038(1)	Cu(1A)–N(4A)	2.007(3)
Co(1)–N(1)	2.091(2)	Cu(1A)–O(5A)	1.954(3)
Co(1)–O(6)	2.103(1)	Cu(1A)–O(6A)	2.358(4)
S(1)–O(2)	1.442(1)	S(1A)–O(3A)	1.432(3)
S(1)–O(3)	1.431(1)	S(1A)–O(4A)	1.436(3)
S(1)–N(4)	1.587(2)	S(1A)–N(2A)	1.598(3)
S(1)–C(7)	1.782(3)	S(1A)–C(6A)	1.786(4)
O(1)–C(6)	1.255(3)	N(2A)–C(7A)	1.338(5)
N(3)–C(5)	1.379(3)	O(5A)–C(7A)	1.256(4)
N(3)–C(6)	1.388(3)	N(3A)–C(8A)	1.375(4)
N(4)–C(6)	1.334(3)	N(3A)–C(7A)	1.378(4)
O(1)–Co(1)–O(1A)	180.0(8)	O(5A–Cu(1A)–O(5AA)	180.0(1)
N(1)–Co(1)–N(1A)	180.0(1)	N(4A)–Cu(1)–N(4AA)	180.0(7)
O(6)–Co(1)–O(6A)	180.0(5)	O(6A)–Cu(1)–O(6AA)	180.0(7)
O(1)–Co(1)–N(1A)	95.0(8)	O(5A)–Cu(1)–N(4A)	87.6(1)
O(1)–Co(1)–N(1)	84.9(8)	O(5A)–Cu(1)–N(4AA)	92.3 (1)
O(1)–Co(1)–O(6)	89.3(4)	O(5AA)–Cu(1)–O(6AA)	95.2(1)
O(1A)–Co(1)–O(6)	90.7(4)	O(5A)–Cu(1)-O(6AA)	84.7(1)
N(1)–Co(1)–O(6)	89.3(3)	N(4AA)–Cu(1)–O(6AA)	91.7 (1)
N(1)–Co(1)–O(6A)	90.7(3)	N(4A)–Cu(1)–O(6AA)	88.2(1)

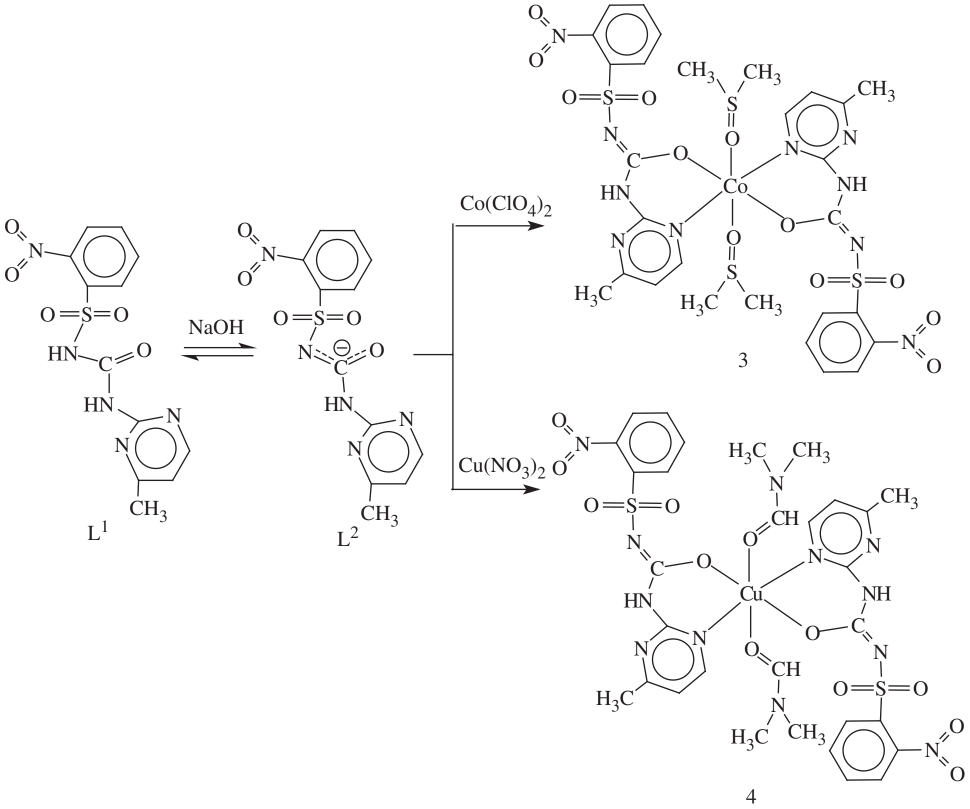
Table 2. Summary of crystallographic data for **3** and **4**.

	3	**4**
Chemical formula	$C_{28}H_{32}CoN_{10}O_{12}S_4$	$C_{30}H_{34}CuN_{12}O_{12}S_2$
Fw	887.81	882.38
Cryst. Syst.	Monoclinic	Triclinic
Space group	$P\ 21/c$	$P\bar{1}$
a (Å)	11.584(5)	10.811(1)
b (Å)	14.176(6)	10.822(1)
c (Å)	12.237(5)	16.198(2)
α(°)	90	87.736(2)
β(°)	111.524(5)	86.880(2)
γ(°)	90	86.860(2)
V(Å^3)	1869.3(1)	1888.4(4)
Z	2	1
D_{Calcd}(Mg m^{-3})	1.577	1.552
Abs coeff. (mm^{-1})	0.756	0.766
F(000)	914	910
Cryst. size (mm)	0.25 × 0.24 × 0.23	0.22 × 0.18 × 0.16
$\theta_{\min}$, $\theta_{\max}$(°)	2.29, 27.76	1.89, 25.03
T/K	293(2)	293(2)
No. of data collected	12189	10377
No. of unique data	4351	6586
No. of refined params.	292	522
Goodness-of-fit on F^2 [a]	1.088	1.058
Final R indices[b] [$I > 2\sigma(I)$]		
R_1	0.0424	0.0487
wR_2	0.1053	0.1230
R indices (all data)		
R_1	0.0695	0.0796
wR_2	0.1141	0.1359

[a] $\mathrm{Goof} = [\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined.
[b] $\mathrm{R1} = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$; $\mathrm{wR2} = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

generate an intermediate (**L^2**) which can coordinate with Co(II) in DMSO/H_2O or Cu(II) in DMF/H_2O solution, respectively, to form [Co(L^2)$_2$(DMSO)$_2$] (**3**) and [Cu(L^2)$_2$(DMF)$_2$] (**4**) (L^2 = deprotonated *N*-[2′-(4-methyl)pyrimidinyl]-2-nitrobenzensulfonylurea, DMSO = dimethyl sulfoxide, DMF = dimethylformamide).

Crystal analyses show that **3** and **4** have similar molecular structures as depicted in figures 1(a) and 2(a). In **3** and **4**, **L^2** is a bidentate ligand and two solvent molecules (two DMSOs for **3** and two DMFs for **4**) coordinate with Co(II) for **3** and Cu(II) for **4** to form octahedral geometry, where two nitrogen donors (N(4) and N(4A) for **3** and N(4A) and N(4AA) for **4**) and two oxygen donors (O(5) and O(5A) for **3** and O(5A) and O(5AA) for **4**) from two **L^2** occupy the square plane, and two oxygen donors from two solvent molecules (O(6) and O(6A) from two DMSOs for **3** and O(6A) and O(6AA) from two DMFs for **4**) coordinate to the axial sites of the octahedron. The N–C distances (N(4)–C(6) = 1.334(3) Å for **3** and N(2A)–C(7A) = 1.338(5) Å for **4**) are shorter than N–C single bonds (1.470 Å), but longer than N–C double bonds (1.270 Å). The C–O distances (C(6)–O(1) = 1.255(3) Å for **3** and C(7A)–O(5A) = 1.256(4) Å for **4**) are shorter than C–O single bonds (1.41 Å), but longer than C–O double bonds (1.14 Å) [12, 13], showing delocalization among N–C–O. In **3** or **4**, the two pyrimidine rings bonded to M(II) centers are parallel, and two benzene rings from two different **L^2** are also parallel. The pyrimidine ring and benzene ring form the dihedral angles of 68.1° for **3** and 73.6° for **4**.



Scheme 1. Formation of **3** and **4**.

In **3** and **4**, the O–M–O and N–M–N (the O(1)–Co–O(1A), O(6)–Co–O(6A) and N(1)–Co–N(1A) for **3**, and the O(5A)–Cu(1A)–O(5AA), O(6A)–Cu(1A)–O(6AA) and N(4A)–Cu(1A)–N(4AA) for **4**) are linear. In **3** the Co(1)–N(1), Co(1)–O(1) and Co(1)–O(6) bond lengths are the same as Co(1)–N(1A), Co(1)–O(1A) and Co(1)–O(6A), respectively. In **4** the Cu(1A)–N(4A), Cu(1A)–O(5A) and Cu(1A)–O(6A) bond lengths are also the same as Cu(1A)–N(4AA), Cu(1A)–O(5AA) and Cu(1A)–O(6AA), respectively. Thus, the crystal structures of **3** and **4** are symmetrical. In **3** and **4**, one M–O distance (Co(1)–O(6) = 2.109(14) Å for **3** and Cu(1A)–O(6A) = 2.358(4) Å for **4**) is longer than M–O (Co(1)– O(1) = 2.038 (1) Å for **3** and Cu(1A)–O(5A) = 1.954(3) Å for **4**). The bond angles around metal center range from 84 to 95°.

In stacking diagram of **3** and **4** (figures 1(b) and 2(b)) 1-D infinite chains are formed via C–H ··· O intermolecular hydrogen bonds [14] (table 3) between adjacent entities. In **3** there exist C–H ··· O intermolecular hydrogen bonds, where oxygen atom is from NO_2 and hydrogen is from the CH_3 on DMSO. In **4** there exist two types of C–H ··· O intermolecular hydrogen bonds, where oxygens are from NO_2 and sulfonyl group, respectively, and hydrogen is from CH_3 on benzene ring.

In **3** the DMSO molecules bonded to the metal are disordered over two positions and were refined with anisotropic displacement parameters and with O–S, S–C and C–H

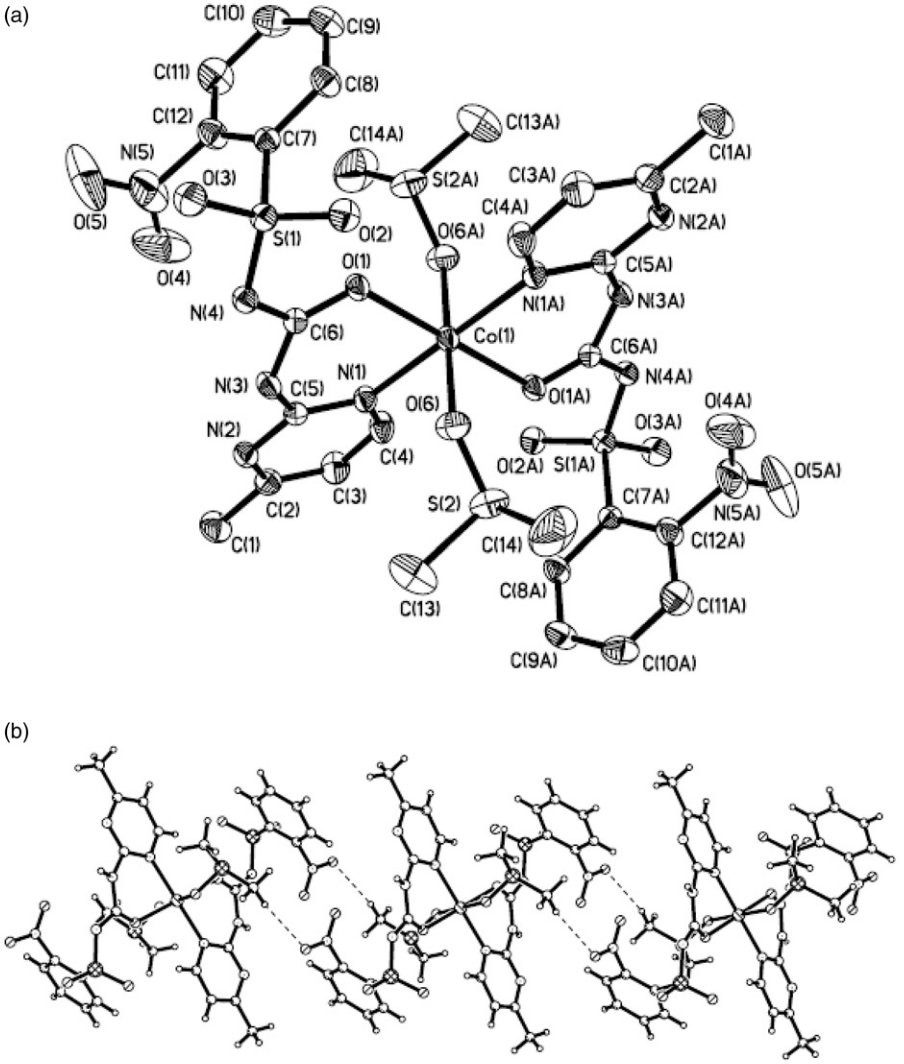


Figure 1. (a) Perspective view of **3** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity. (b) The 1-D chains by hydrogen-bonding interactions in **3**.

distances restrained to 1.499(7) Å, 1.794(6) Å and 0.960(1) Å, respectively. The occupancy factors are 0.663(1) and 0.337(1), respectively.

3.2. *Fluorescent emission spectra of L^1, 3 and 4*

The fluorescent emission spectra of $\mathbf{L^1}$, **3** and **4** in dichloromethane (5.0×10^{-6} M) are shown in figure 3. For $\mathbf{L^1}$, the maximum emission peaks are at 330 and 340 nm, from intraligand $\pi \rightarrow \pi^*$ transitions. In contrast to $\mathbf{L^1}$, **3** and **4** have only one broad emission band at 335 and 338 nm, respectively, assigned to ligand-to-metal-charge-transfer bands

Table 3. H-bonding geometry (Å, °) for **3** and **4**.

	D–H···A	D–H	H···A	D···A	D–H···A
3	C–H···O^{i}	0.959	2.377	3.249	150.9
4	C–H···O^{ii}	0.961	2.476	3.314	145.6
	C–H···O	0.959	2.583	3.535	171.8

Symmetry code: (i): $1+x$, $0.5-y$, $0.5+z$; (ii): $1-x$, $1-y$, $-z$.

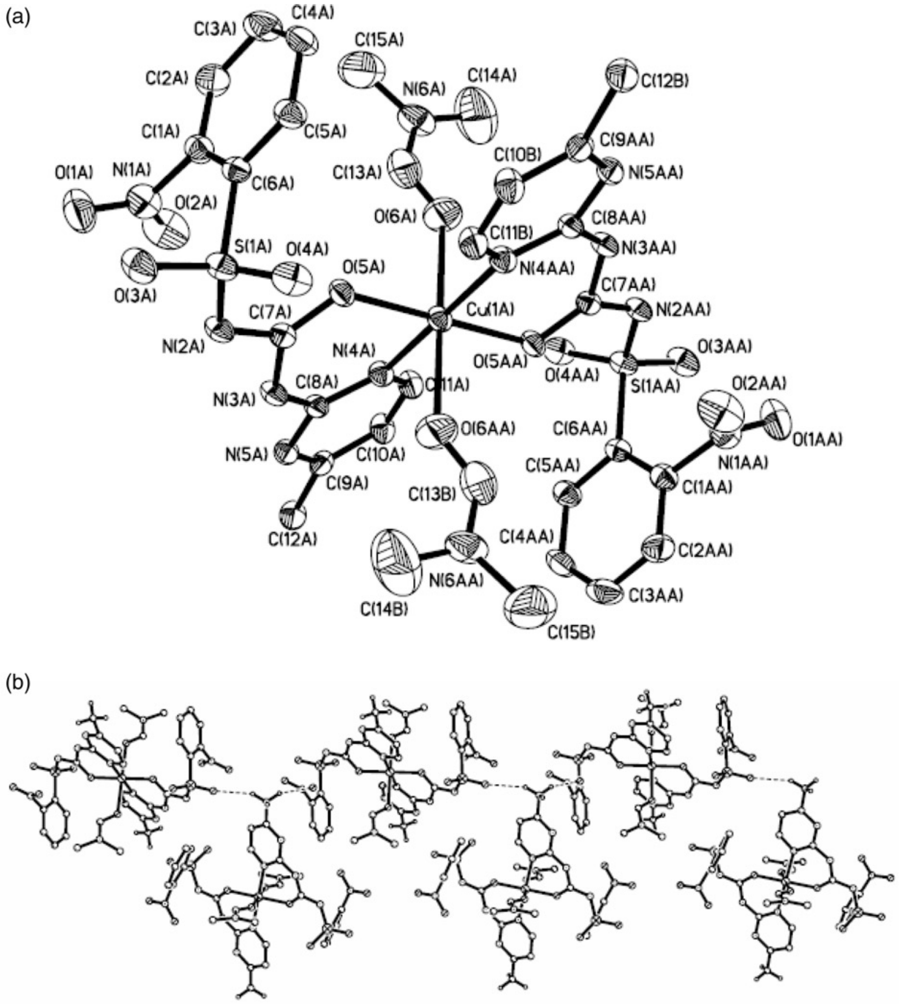


Figure 2. (a) Perspectiveview of **4** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity. (b) The 1-D chains by hydrogen-bonding interactions in **4**.

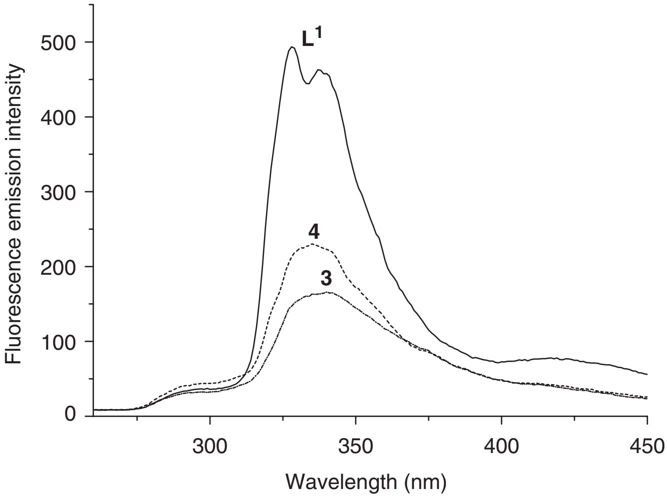


Figure 3. Emission spectra of $\mathbf{L}^1$ (—), **3** (----) and **4** (- - -) at 298 K upon excitation at 256 nm in CH_2Cl_2 (5.0×10^{-6} M).

(LMCT) [15]. The fluorescence emissions of **3** and **4** are weaker than that of $\mathbf{L}^1$, which can be attributed to the electron-withdrawing effect of cobalt(II) and copper(II). These results show that such metal complexes might be good candidates for photoactive materials [16].

3.3. *Thermogravimetric analyses of 3 and 4*

Complexes **3** and **4** are air stable at ambient conditions and thermogravimetric experiments were performed to explore their thermal stability. The TGA curve of **3** reveals that the complex starts to decompose beyond 210°C with one step of weight loss (peaks at 255°C), and does not stop until heating ends at 800°C. The loss of coordinated DMSO moieties is not observed separately, indicating strong coordination to Co(II). The TGA curve of **4** suggests that the complex starts to decompose beyond 100°C with two weight loss steps (peaks at 214°C and 258°C) and does not stop until heating ends at 800°C.

4. Conclusion

Two new cobalt(II) and copper(II) complexes with deprotonated *N*-[2′-(4-methyl)pyrimidinyl]-2-nitrobenzenesulfonylurea have been synthesized and characterized. In the complexes, the deprotonated sulfonylurea is a bidentate ligand and two solvent molecules (DMSO or DMF) coordinate with metal center to complete octahedral geometry. Further studies on complexes from $\mathbf{L}^1$ and analogous precursors are underway.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 661145 for **3** and 661144 for **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] J.E. Franz, C. Osuch. *J. Org. Chem.*, **29**, 2592 (1964).
[2] H.C. Lee. EP 162723, **11**, 27 (1985).
[3] C.C. Chen, T. Stanley. EP 0304282A1, **2**, 22 (1989).
[4] Z.Q. Wang, F.C. Sun, R.Q. Li. *Chinese Patent 98113985X*, **5**, 12 (1988).
[5] T.P. Gandhi, M.N. Jindal. *Arzneim.-Forsch.*, **21**, 968 (1971).
[6] W. Levinson, H. Oppermann, J. Jackson. *Biochim. Biophys. Acta*, **606**, 170 (1980).
[7] D.P. Kessissoglou, G.E. Manoussakis, A.G. Hatzidimitriou, M.G. Kanatzidispp. *Inorg. Chem.*, **26**, 1395 (1987).
[8] A.G. Hatzidimitriou, D.P. Kessissoglou, G.E. Manoussakis, P.N. Kourounakis, G. Economidis. *J. Inorg. Biochem.*, **39**, 263 (1990).
[9] SMART 5.0 and SAINT 4.0 for Windows NT, Area Detector Control and Integration Software, Bruker Analytical X-Ray Systems, Inc., Madison, WI, USA (1998).
[10] G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1996).
[11] G.M. Sheldrick. *SHELXTL 5.10 for Windows NT, Structure Determination Software*, Bruker Analytical X-Ray Systems, Inc., Madison, WI, USA (1997).
[12] Y. Li, Z.X. Zhang, K.C. Li, W.D. Song, X.B. Cui, L.Y. Pan. *J. Mol. Struct.*, **843**, 102 (2007).
[13] Q.X. Liu, X.J. Zhao, X.M. Wu, J.H. Guo, X.G. Wang. *J. Organomet. Chem.*, **692**, 5671 (2007).
[14] (a) C.M.R. Juan, B. Lee. *Coord. Chem. Rev.*, **183**, 43 (1999); (b) R.T.N. Guru. *Coord. Chem. Rev.*, **183**, 81 (1999); (c) E.S. Alekseyeva, A.S. Batasanov, L.A. Boyd, M.A. Fox, T.G. Hibbert, J.A.K. Howard, J.A.H. MacBride, A. Mackinnon, K. Wade. *Dalton Trans.*, 475 (2003); (d) G.R. Desiraju. *Acc. Chem. Res.*, **29**, 441 (1996).
[15] (a) R. Bertoncello, M. Bettinelli, M. Casarin, A. Gulino, E. Tondello, A. Vittadini. *Inorg. Chem.*, **31**, 1558 (1992); (b) J. Tao, M.L. Tong, J.X. Shi, X.M. Chen, S.W. Ng. *Chem. Commun.*, 2043 (2000).
[16] (a) B.P. de Silva, H.Q.N. Lgunaratne, T.L. Gunnlangsson, A.J.M. Unzley, C.P. McCoy, J.T. Rademacher, T.E. Rice. *Chem. Rev.*, **97**, 1515 (1997); (b) V.W.W. Yam, K.L. Yu, K.M.C. Wong, K.K. Cheung. *Organometallics*, **20**, 721 (2001); (c) K.J. Wei, Y.S. Xie, J. Ni, M. Zhang, Q.L. Liu. *Cryst. Growth Des.*, **6**, 1341 (2006); (d) J.P. Desvergne, F. Fages, H. Bouas-Laurent, P. Marsau. *Pure and Appl. Chem.*, **64**, 1231 (1992); (e) S.C. Chan, M.C.W. Chan, Y. Wang, C.M. Che, K.K. Cheung, N. Zhu. *Chem. Eur. J.*, **7**, 4180 (2001).