Synthesis, Spectral, Thermal, and Electrical Conductivity Studies of Cobalt(II) and Copper(II) Sulfadiazine Complexes

K. Y. EL-BARADIE* and M. GABER**

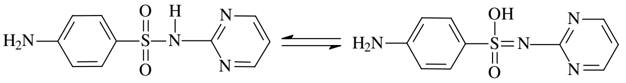
Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt
e-mail: kelbaradie@hotmail.com

Received 29 April 2002

Coordination compounds of Co(II) and Cu(II) ions with sulfadiazine have been prepared and characterized by elemental analysis, molar conductivity, magnetic moments, and spectral studies. The IR spectra show that the ligand acts as a monovalent bidentate or neutral bidentate depending on the metal salt used and the type of the reaction. The thermal decomposition of the complexes has been studied by thermogravimetric and differential thermal analysis. The activation energy of the thermal decomposition processes is determined. The electrical conductivity of the ligand and its metal complexes is determined at different temperatures.

Sulfonamides constitute a class of drugs, which are frequently used in pharmaceutical preparations, especially in veterinary practice. Sulfadiazine is one of the sulfonamides used in the treatment of urinary tract infections, pneumocystic pneumonia, chronic bronchitis, meningococcal meningitis, acute otitis media, and toxoplasmosis [1]. Interests in the field of sulfa drugs study are fundamental not only for gaining some insight into the determination of sulfa in pharmaceutical samples [2—6] but also for obtaining information about the structure, as well as the chelating behaviour of the sulfa drugs [7—13].

In continuation of our work on the behaviour of sulfur-containing ligands [7—9], we describe here the synthesis and characterization of Co(II) and Cu(II) complexes with sulfadiazine as ligand.



The prepared compounds are listed in Table 1 and the formulae given are in agreement with the chemical analyses. Coordination of the neutral form of the ligand occurs when Cu(II) chloride is used for the preparation of the complex. Other salts provide complexes with anionic form of the ligand. The molar conductivities of the resulting complexes in DMF ($c = 10^{-3}$ mol dm^{-3}) at 25 ℃ are in the range 15.2—20.1 S cm^2 mol^{-1} indicating that the complexes are nonelectrolytes [14], accordingly, the salt anions whenever present would be involved in the coordination sphere.

The most important IR bands of the ligand as well as its bonding sites (Table 2) have been determined by careful comparison of both the ligand and its complexes and considering the previous works [7—9]. The comparison shows that sulfadiazine behaves as monobasic or neutral bidentate ligand coordinating *via* the S═O group and pyrimidine nitrogen. This behaviour is supported by the following evidence.

The ν(NH) of the free ligand at $\tilde{\nu} = 3256$ cm^{-1} disappeared from the spectra of all complexes except Cu(II) complex *II* indicating the covalent nature of the metal oxygen bond with simultaneous appearance of a new band in the region 502—525 cm^{-1} assigned to M—O bond [15, 16]. The disappearance of the band at 722 cm^{-1} due to δ(NH) out-of-plane deformation may be taken as evidence for enolization of the hydrogen of NH group [17] to the adjacent sulfonyl group.

The ν(C═N) band of the pyrimidine ring is shifted to lower wavenumber suggesting that one nitrogen atom of this ring is taking part in complex formation. The appearance of bands in the $\tilde{\nu}$ region 266—341 cm^{-1} assigned to ν(M—N) pyridine-like imine nitrogen [9] supports the involvement of this nitrogen atom in complex formation.

The chloro complex exhibits a band at 305 cm^{-1} assigned to Cu—Cl bond [18] while the acetato complexes *I* and *III* show bands at 1630 cm^{-1}, 1535 cm^{-1} and 1625 cm^{-1}, 1525 cm^{-1} assignable to monodentate acetate group [19] for complexes *I* and *III,* respec-

---

*The author to whom the correspondence should be addressed.

***Present address*: Department of Chemistry, College of Education, King Faisal University, P.O. Box 1759 Hofuf, 31982 Saudi Arabia.

Table 1. Analytical Data and Molar Conductivity Values for Sulfadiazine (L) Complexes

	Complex	Formula	w_i(calc.)/% (w_i(found)/%)				Λ
			C	H	N	M	S cm^2 mol^{-1}
I	[CoL(AcO)(H$_2$O)$_3$]	$C_{12}H_{18}N_4O_7SCo$	34.2 (34.0)	4.3 (4.1)	13.3 (13.0)	14.0 (13.9)	15.2
II	[CuLCl$_2$(H$_2$O)$_2$]H$_2$O	$C_{10}H_{16}N_4O_5SCuCl_2$	27.4 (27.1)	3.7 (3.6)	12.8 (12.5)	14.5 (14.4)	16.8
III	[CuL(AcO)(H$_2$O)]	$C_{12}H_{14}N_4O_5SCu$	37.0 (36.7)	3.6 (3.5)	14.4 (14.2)	16.3 (16.1)	14.0
IV	[CuL(NO$_3$)(H$_2$O)]	$C_{10}H_{11}N_5O_6SCu$	30.6 (30.3)	2.8 (2.6)	17.8 (17.5)	16.2 (16.0)	14.2
V	[CuL$_2$]Ac	$C_{23}H_{24}N_8O_5S_2Cu$	44.6 (44.4)	3.9 (3.6)	18.1 (17.8)	10.3 (10.1)	13.6
VI	[CuL$_2$L′]	$C_{32}H_{26}N_{10}O_4S_2Cu$	51.8 (51.5)	3.5 (3.3)	18.9 (18.6)	8.6 (8.5)	10.2
VII	[CuL$_2$L″]	$C_{38}H_{33}N_8O_4S_2PCu$	55.4 (55.1)	4.0 (3.8)	13.6 (13.3)	7.7 (7.5)	10.5

Ac – acetone, L′ – 1,10-phenanthroline, L″ – triphenyl phosphine (Ph$_3$P).

Table 2. Infrared, Electronic, ESR Spectral Data and Magnetic Moment Values for Sulfadiazine Complexes

Compound	IR spectra ($\tilde{\nu}$/cm^{-1})				μ_{eff}/BM	d—d transition $\tilde{\nu}$/cm^{-1}		ESR spectra			
	H$_2$O	C═N	M—N	M—O				g	g_1	g_{av}	G
Lig.	–	1582	–	–	–						
I	3426	1576	341	502	4.75	17360	20000				
II	3425	1577	317	520	1.83	14286		2.26146	2.07289	2.1376	4.0
III	3451	1549	270	525	1.85	19418	22893				
IV	3480	1576	275	520	1.69	19607	22893	2.12969	2.08054	2.09705	2.5
V	–	1549	270	525	1.81	19379	22727				
VI	–	1537	266	523	1.77	14923		2.29212	2.06466	2.14316	4.5
VII	–	1547	321	525	1.78	16129					

tively. The IR spectrum of the nitrate complex *IV* exhibits characteristic vibrational frequencies of coordinated nitrate group, which is suggested by new bands at 1325 cm^{-1} and 1295 cm^{-1} due to ν_4 and ν_1 vibrations of the nitrate group of $C_{2\nu}$ symmetry [20]. The moderate band at 799 cm^{-1} due to the ν_2 vibration of the nitrate group stands as additional evidence for the presence in wavenumber between the two highest frequencies about 30 cm^{-1} indicating that the coordinated nitrates are monodentate [15]. In addition a band appears at 350 cm^{-1} which can be assigned to ν(Cu—O) supporting the monodentate character for coordinated nitrate group [21]. Also, the IR spectrum of complex *V* exhibits an additional band at 1659 cm^{-1} assigned to the stretching mode of C═O group as a result of the presence of the acetone molecule. The spectra of the metal complexes *I*—*IV* exhibit characteristic bands of coordinated water in the regions $\tilde{\nu}$ = 3426—3480 cm^{-1}, 842—860 cm^{-1}, and 794—798 cm^{-1} assigned to ν(OH), f_{r}(H$_2$O), and f_{w}(H$_2$O) vibrations, respectively [15].

The room temperature magnetic moments and the electronic spectral data of the complexes are listed in Table 2. The magnetic moment of Co(II) complex (4.75 BM) is near the spin value for the high-spin octahedral complex [22]. The electronic spectrum of the Co(II) complex shows two bands at 17360 cm^{-1} and 20000 cm^{-1} assigned to $^4T_{1\text{g}}$(F) → $^4A_{2\text{g}}$(F) (ν_2) and $^4T_{1\text{g}}$(F) → $^4T_{1\text{g}}$(P) (ν_3) transitions, respectively.

The magnetic moments of Cu(II) complexes *II*—*VII* are in the range expected for monomeric Cu(II) complexes [23]. The electronic spectra of Cu(II) complexes *III*—*V* exhibit bands in the range $\tilde{\nu}$ = 19379—22843 cm^{-1} corresponding to the $^2B_{1\text{g}} \rightarrow {}^2E_{\text{g}}$ transition. The intensity of the bands and the magnetic moment values support the square-planar geometry for Cu(II) complexes *III*—*V* [24, 25]. The Nujol mull spectra of Cu(II) complexes *II* and *VI* exhibit bands at 14286 cm^{-1} and 14923 cm^{-1}, respectively, assigned to $^2B_{1\text{g}} \rightarrow {}^2E_{\text{g}}$ transition arising from highly distorted octahedral arrangement. The spectrum (band at 16129 cm^{-1}) and the magentic moment (1.78 BM) of Cu(II) complex *VII* are similar to those reported for five-coordinated square-pyramidal structure.

The ESR spectra of the Cu(II) complexes were recorded at room temperature. The $g_{//}$ and $g_{/}$ have been calculated and observed in the range 2.19895—2.29212 and 2.06466—2.08054, respectively, which supports the idea that $d_{\text{X}^2-\text{Y}^2}$ [26] may be the ground state ($g_{//} > g_{/} > 2.0023$).

The parameter G has been calculated from the relation

$$G = (g_{//} - 2)/(g_1 - 2)$$

The value for G when being larger than four indicates that considerable exchange interaction is absent. In the present case, the axial symmetry parameter G for complex *VI* is larger than four denoting the absence of Cu—Cu exchanges. For complex *IV* the G value

Table 3. Thermal Decomposition and Electrical Conductivity Data of Sulfadiazine Complexes

Process	Δt/°C	Mass fraction loss/%		DTA		Semiconductor		Metal	
	TGA	TGA	Calc.	t(Peak) °C	E_a (kJ mol^{-1})	Δt °C	E_a (kJ mol^{-1})	Δt °C	E_a (kJ mol^{-1})
$[CoL(AcO)(H_2O)_3] \rightarrow [CoL(AcO)H_2O]$	243—283	8.37	8.55	Endo (244)	–	20—79	3.86	74—100	6.54
$[CoL(AcO)H_2O] \rightarrow CoL$	290—484	19.6	20.0	Exo (336)	–	100—127	6.0	127—165	11.4
$CoL \rightarrow CoO$	500—700	13.8	14.0	Exo (580)	–				
$[CuLCl_2(H_2O)_2]H_2O \rightarrow [CuLCl_2(H_2O)_2]$	25—100	3.95	4.10	Endo (128)	–	25—66	8.71	81—97	12.8
$[CuLCl_2(H_2O)_2] \rightarrow CuLCl_2$	175—242	8.42	8.56	Endo (160)	–	142—156	28.0		
$CuLCl_2 \rightarrow CuL$	354—539	16.09	16.19	Exo (237)	–				
$CuL \rightarrow CuO$	540—700	14.20	14.48	Exo (509)	17.13				
$[CuL(AcO)(H_2O)] \rightarrow [CuL(AcO)]$	239—251	4.70	4.62	Endo (163)	–	–	–	55—84	0.4
$[CuL(AcO)] \rightarrow [CuL]$	251—407	15.35	15.88	Exo (307)	–	–	–	88—143	2.1
$[CuL] \rightarrow CuO$	415—510	16.10	16.30	Exo (433)	27.72				
$[CuL(NO_3)(H_2O)] \rightarrow [CuL(NO_3)]$	80—148	4.46	4.60	Endo (113)					
$[CuL(NO_3)] \rightarrow [CuL]$	148—237	16.48	16.56	Exo (217)					
$[CuL] \rightarrow CuO$	300—615	16.00	16.20	Exo (303)	15.3				
$[CuL]Ac \rightarrow [CuL_2]$	25—150	9.3	9.4	Exo (303)	–				
$[CuL_2] \rightarrow CuL$	235—394	50.1	50.4		–				
$CuL \rightarrow CuO$	465—700	12.5	12.8	Exo (562)	40.23				
$CuL_2L' \rightarrow CuL_2$	200—400	23.9	24.3	Exo (430)					
$CuL_2 \rightarrow CuO$	450—750	10.5	10.7	Exo (631)	61.97				
$CuL_2L'' \rightarrow CuL_2$	245—400	31.40	31.80	Exo (420)					
$CuL_2 \rightarrow CuO$	455—600	9.43	9.65	Exo (587)	48.60				
L	–	–	–	–	–	25—45 72—110	13.8 7.4	45—72	8.0

L′ – 1,10-phenanthroline, L″ – triphenyl phosphine.

is less than four suggesting the existence of Cu—Cu exchange interactions [27]. For complex *II*, the value of G denotes weak or even the absence of Cu—Cu interactions.

From the TGA curves, the mass loss was calculated for the different steps and compared with those theoretically calculated for the suggested formula based on the results of elemental analyses. Also, TGA suggested the formation of the metal oxide as the end product from which the metal content can be calculated and compared with that obtained from analytical determination.

The mass losses, relative residues, temperature ranges, and final decomposition products observed in each step of TGA/DTA curves for the solid complexes are given in Table 3. The results show that complexes *I*—*IV* decompose mainly in three steps. The first step within the temperature range 25—283 °C brings about a mass fraction loss ranging from 3.95—8.42 % with an endothermic peak within the range 113—163 °C. This mass loss corresponds to elimination of hydration and/or coordinated water molecules. The second step within the temperature range 150—539 °C with exothermic peak at 217—307 °C corresponds to the removal of the anion attached to the metal ion. The final decomposition step in the temperature range 350—700 °C with broad exothermic peak within the range 303—509°C includes the thermal decomposition of the complexes [31] and loss of their organic portion with the formation of the metal oxide from which the metal content was calculated.

The values of the activation energies (E_a) for the decomposition processes are evaluated using the method of *Piloyan et al.* [28]. Arrhenius plots were constructed and E_a values are obtained from the slope as listed in Table 3 using Reich's empirical relation [29]; the order of reaction (n) of the thermal process is given by $n = 1.26\sqrt{a/b}$ where (a/b) is the slope factor of the peak. In general, the data ($n = 0.82$—1.2) indicate that the process follows the first-order kinetics.

The current (I) was measured at the applied voltage V to establish the I—V characteristics. The $\log\{I\}$ *vs.* $\log\{V\}$ plots for complexes *I*—*III* indicate that the proportionality $I \sim V^n$ is obtained with $n \approx 1$. Therefore it is concluded that the complexes obey Ohm's law.

$$\sigma = \sigma_0 \exp\left(-\Delta E/kT\right)$$

where σ_0 , ΔE, and k are the conductivity constant, activation energy, and Boltzman constant.

From the linear relationship ΔE can be calculated. The conductivity of the free ligand increases with increasing temperature, hence it exhibits semiconducting properties. In addition, the free ligand has two modes of conduction and therefore it has two activation energy values ΔE_1 and ΔE_2 with two transition temperatures at 45 ℃ and 72 ℃. The discontinuity in the semiconducting region can be ascribed to a molecular rearrangement [30]. The first step in the conduction process is due to electronic conduction *via* π-electron delocalization while at higher temperatures, the conduction is due to electronic excitation from the higher filled π-molecular orbitals to the lower unfilled π^*-molecular orbitals [31]. Thus, the electron is assumed to tunnel to an equivalent empty level of a neighbouring molecule in the anodic direction. Alternatively, hopping conduction mechanism might prevail.

The electrical conductivity of the Co(II) complex exhibits semiconducting behaviour in the temperature ranges 25—79 ℃ and 100—127 ℃ while a metallic behaviour appears in the temperature ranges 79—100 ℃ and 127—163 ℃ due to the loss of water molecules and lattice rearrangement with changing the geometrical structure of the complexes. Also, the data indicate that the conductivity of Cu(II) complex *III* decreases with the rise of temperature (55—143 ℃), *i.e.* it shows metallic behaviour which can be explained by the cationic disproportionation [31].

The electrical conductivity of Cu(II) complex *II* increases with temperature in the lower (25—66 ℃) and higher (142—156 ℃) temperature range, with the shallow behaviour in the temperature ranges 46—81 ℃ and 97—142 ℃ which can be attributed to the loss of coordinated water and thermal keto $\rightleftharpoons$ enol tautomerism [38].

EXPERIMENTAL

All compounds used were pure grade BDH products.

The equipments and the methods employed in the present study were the same as reported earlier [32—37]. C, H, and N contents were measured at the Microanalytical unit of the Cairo University. The metals were determined by complexometric titration against EDTA [38]. Molar conductivity measurements were made in DMF ($c = 10^{-3}$ mol dm^{-3}) using a YSI model 32 conductance meter. Magnetic moments were determined on a Johnson—Matthey magnetic susceptibility balance. The IR spectra of the ligand and its metal complexes were obtained as KBr pellets by a Perkin—Elmer 1430 IR spectrophotometer. The electronic spectra in Nujol mull were recorded with a Shimadzu 240 UV-visible spectrophotometer. The ESR spectra were recorded with the aid of Jeol JES spectrophotometer. The thermal study (TGA and DTA) was achieved using Shimadzu TG 50 thermal analyzer. The electrical conductivity was measured using super Megohmmeter (Model RM 170). The samples were in the form of discs of 13 mm diameter and 1—3 mm thickness which were pressed under a pressure of 30 MPa. Good contact was achieved by liquid silver painting on the two opposite surfaces of each disc. The temperature was measured in air using Cu(Cu-Ni) thermocouple placed close to the sample.

The metal complexes were prepared by mixing the stoichiometric quantities (0.5 m mol) of the hydrated metal salt (chloride, acetate or nitrate) in 25 cm^3 of absolute ethanol to the ligand (0.5 m mol) in 50 cm^3 of the same solvent. The mixture was refluxed on a water bath for 6 h. On cooling, the separated complexes were filtered off, washed with hot ethanol and dried in vacuum desiccator over anhydrous $CaCl_2$.

The electrochemical technique used for preparing some complexes was essentially the same as reported previously [16, 17] where the pure copper metal was used as the anode and Pt as the cathode while the electrolyte was made of the ligand (0.5 g) dissolved in the mixture of acetone (20 cm^3) and ethanol (5 cm^3) with 25 mg of Et_4NClO_4. The anodic dissolution of Cu from the anode in the electrolyte amounted to 64 mg at 10 V and 20 mA current strength. The precipitated solid complexes were collected, washed several times with acetone—ethanol mixture, and then dried in vacuum desiccator. For adduct complexes 0.18 g of 1,10-phenanthroline and 0.28 g of Ph_3P were added.

REFERENCES

1. *Sulfonamides* in *American Hospital Formulary Service Drug Information.* (McEvoy, G. K., Editor.) P. 472. American Hospital Formulary Service, Bethesda, 1993.
2. Tseng, S. S. and Smith, T. J., *Anal. Lett. 27*, 1507 (1994).
3. Amin, A. S., El-Sayed, G. O., and Issa, Y. M., *Microchem. J. 51*, 367 (1995) and references cited therein.
4. Issa, Y. M., El-Ansary, A. L., and Selim, W., *Anal. Lett. 31*, 131 (1998).
5. Kargosha, K. and Ahmadi, S. H., *Anal. Lett. 32,* 1613 (1999).
6. Cruces-Blanco, C., Segura-Carretero, A., Fernandez-Peinado, S., Roman-Ceba, M., and Fernandez-Guttierrez, A., *Fresenius' J. Anal. Chem. 365*, 444 (1992).
7. Gaber, M., *Delta J. Sci. 14*, 924 (1990).
8. Gaber, M., Mabrouk, H. E., Shaibi, Y. M., and Ba-Issa, A. A.,*Thermochim. Acta 207,* 239 (1992).
9. Elmorsi, M. A. and Gaber, M., *J. Chim. Phys. 93,* 1556 (1996).
10. Hosny, W. M., *Synth. React. Inorg. Met.-Org. Chem. 29*, 361 (1999).
11. Maurya, R. C. and Patel, P., *Spectrosc. Lett. 32*, 213 (1999).
12. El-Bindary, A. A. and El-Sonbati, A. Z., *Pol. J. Chem. 74*, 615 (2000).
13. Gaber, M., Mabrouk, H. E., and Al-Shihry, S. S., *Egypt J. Chem.*, in press.
14. Geary, W. J., *Coord. Chem. Rev. 7,* 81 (1971).
15. Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds.* 4th Edition, p. 332. Wiley, New York, 1986.
16. Teatia, M. P., Singh, I., Singh, P., and Rana, V. B., *Synth. React. Inorg. Met.-Org. Chem. 14*, 603 (1984).

17. Nawar, N. and Hosny, N. M., *Transition Met. Chem. 25*, 1 (2000).
18. Swearing, J. K. and West, D. X., *Transition Met. Chem. 26*, 252 (2001).
19. Kaul, B. B. and Pandeya, K. B., *J. Inorg. Nucl. Chem. 40*, 1035 (1977).
20. Landers, A. E. and Phillips, D. J., *Inorg. Chim. Acta 74*, 43 (1983); Catehouse, B. M., Livingstone, S. E., and Nyhoin, R. S., *J. Inorg. Nucl. Chem. 8*, 75 (1958).
21. Nipp, C. A. and West, D. X., *Synth. React. Inorg. Met.-Org. Chem. 15*, 1139 (1985) and references cited therein.
22. Prebi, C. and Tosi, G., *Aust. J. Chem. 29*, 543 (1976).
23. Palla, G., Pelizzi, V., Preier, G., and Vignall, C., *Gazz. Chim. Ital. 112*, 339 (1982).
24. Faniran, J. A., Patel, K. S., and Nelson, L. O., *J. Inorg. Nucl. Chem. 38,* 77 (1976).
25. Nicolini, M., Pecile, C., and Turco, A., *Coord. Chem. Rev. 1*, 133 (1966).
26. Jain, M. C., Srivastava, A. K., and Jain, P. C., *Inorg. Chim. Acta 23*, 199 (1977).
27. Hathaway, B. J. and Billing, D. E, *Coord. Chem. Rev. 5*, 143 (1970).
28. Piloyan, G. O., Raybchikov, I. D., and Novikova, O. S., *Nature 212*, 1229 (1966).
29. Reigh, T., *J. Inorg. Nucl. Chem. 28,* 1329 (1966).
30. Gutmann, F. and Metschey, A., *J. Chem. Phys. 36*, 2355 (1962).
31. El-Baradie, K. Y, Gaber, M., and Abu-Sekkina, M., *Thermochim. Acta 246,* 175 (1994).
32. Cohen, M. D. and Flavian, S. T., *J. Chem. Soc., B 1967*, 317.
33. Gaber, M., Mabrouk, H. E., and Mounir, M., *Thermochim. Acta 186*, 89 (1991).
34. El-Hefnawy, G. B., El-Trass, A. E., and Gaber, M., *Synth. React. Inorg. Met.-Org. Chem. 22,* 1445 (1992).
35. Mabrouk, H. E., Gaber, M., El-Sonbati, A. Z., and El-Hefnawy, G. B., *Transition Met. Chem. 17,* 1 (1992).
36. Gaber, M., Mabrouk, H. E., Ba-Issa, A. A., and Ayad, M. M., *Monatsh. Chem. 123,* 1089 (1992).
37. Gaber, M., Mabrouk, H. E., Al-Shaibi, Y., and Al-Azab, F. M., *Egypt J. Chem. 40*, 177 (1997).
38. Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis.* Longmans, London, 1961.