

Synthesis, Characterization and Properties of Heterobimetallic Complexes of Zinc(II) Dithiocarbamate Derivatives with Cobalt, Nickel and Copper Metal Ions.

IHSAN A. MUSTAFA, OMAR M. AL-RAMADANY and TALAL A.K. AL-ALLAF*

Department of Chemistry, College of Science, University of Mosul, Mousl, Iraq

Several heterobimetallic complexes of the general formula $[\text{Zn}(\text{R-dtc})_2\text{MCl}_2]_n$, where R-dtc is methyl-, cycloheptyl- or dicyclohexyl-dithiocarbamate, $\text{M}=\text{Co}$, Ni , Cu and $n = 1$ or 2 , have been prepared from the reaction of the precursor compound $\text{Zn}(\text{R-dtc})_2$ (prepared from Zinc(II) salt and the sodium or potassium dithiocarbamate derivative) and the corresponding anhydrous metal salt MCl_2 in non-aqueous solvents and in different molar ratios. The complexes have been characterized physicochemically and spectroscopically. Suggested structures for the complexes have been given and discussed.

INTRODUCTION

The chemistry of dithiocarbamates and their metal ion complexes were an intensive area of study and represent an important target for most researchers due to their chemical and biological importance and hence these were covered by many research articles. It was found that free dithiocarbamates can be used against renal toxicity of cisplatin; *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ ¹. Also metal complexes of dithiocarbamate were showed a good antifungal activity². On the other hand, a numerous metal complexes of dithiocarbamates have been accordingly investigated, with both main group metals, *e.g.*, aluminium and gallium³, tin⁴ and the transition metals, *e.g.*, copper⁵, palladium^{6,7}, nickel⁸, molybdenum and tungsten⁹ and rhenium¹⁰. Because of the importance of the dithiocarbamate derivatives and their metal complexes and as a continuation of our intrinsic interest for studying the type of interaction between metal ions and some sulfur-containing ligands, *e.g.*, platinum group metal complexes with thiourea¹¹, xanthate, dithiocarbamate and dithiophosphate¹², organotin(IV) complexes with xanthate^{13,14} and their biological activities against bacteria and tumour cells¹⁵, we are presenting in this work, the synthesis and characterization of some heterobimetallic complexes of

*Department of Chemistry, Faculty of Basic Sciences, Applied Science University, Amman-11931, Jordan.

E.mail: tatal_al_allaf@hotmail.com

dithiocarbamate with cobalt, nickel and copper derived from Zn(R-dtc)_2 and MCl_2 , where R = methyl, cycloheptyl, dicyclohexyl and $\text{M} = \text{Co, Ni, Cu}$.

EXPERIMENTAL

All the chemicals were of AnalaR grade (BDH, Aldrich or Fluka) and used as such without further purification. The complexes were analysed for carbon, hydrogen and nitrogen using 1106 (Carlo Erba) micro analyser. Infrared absorption spectra were recorded on a Unicam SP-2000 spectrophotometer as CsI discs in the range $4000\text{--}200\text{ cm}^{-1}$. The magnetic susceptibility measurements were made by the Faraday method at room temperature using a Bruker B.M. 6 instrument. The electronic spectra were recorded on a Shimadzu UV-VIS spectrophotometer (range $200\text{--}1100\text{ nm}$), model 160 Koyoto (Japan) using acetonitrile as a solvent.

The salts potassium methyldithiocarbamate K(Me-dtc) sodium cycloheptyl-dithiocarbamate Na(Chep-dtc) and sodium dicyclohexyldithiocarbamate $\text{Na(Chex}_2\text{-dtc)}$ were prepared according to the method described by Brewer *et al.*¹⁶ The compound zinc *bis*-(dithiocarbamate derivative), *i.e.*, Zn(R-dtc)_2 was prepared by the method described by Malik *et al.*¹⁷

Preparation of complexes

$\text{Zn(R-dtc)}_2 \cdot \text{MCl}_2$, $\text{M} = \text{Co, Ni, Cu}$: To a solution of Zn(R-dtc)_2 , (R-dtc = methyl-, cycloheptyl- or dicyclohexyldithiocarbamate) (3 mmol) in dichloromethane (15 mL) was added a solution of anhydrous MCl_2 ($\text{M} = \text{Co, Ni, Cu}$) (3 mmol) in methanol (15 mL) with a vigorous stirring. The reaction mixture was stirred at room temperature for 8–14 h and then filtered. The filtrate was treated with *n*-pentane (15 mL), which after few min. a precipitate started to deposit. This was filtered off, washed with ether and dried under vacuum.

$[\text{Zn(R-dtc)}_2 \cdot \text{MCl}_2]_2$, $\text{M} = \text{Co, Ni, Cu}$: To a solution Zn(R-dtc)_2 , (17 mmol) in dichloromethane (15 mL) was added a solution of anhydrous MCl_2 (12 mmol) in a mixture of tetrahydrofuran (15 mL) and triethyl-orthoformate (3 mL) with a vigorous stirring. The reaction mixture was stirred at room temperature for 8–12 h and then filtered. The filtrate was treated with *n*-pentane (15 mL). The solid thus formed was filtered off, washed several times with ether and dried in vacuum.

RESULTS AND DISCUSSION

The physical properties of potassium or sodium salt of the dithiocarbamate derivatives and their heterobimetallic complexes are listed in Table-1, the IR and magnetic moments data are listed in Table-2, and the electronic spectra and molar conductivities of the complexes are listed in Table-3. The elemental composition of the complexes prepared are correspond to 1 : 1, Zn(R-dtc)_2 : MCl_2 molar ratio, *i.e.*, $[\text{Zn(R-dtc)}_2 \cdot \text{MCl}_2]_n$ ($\text{M} = \text{Co, Ni, Cu}$, $n = 1$ or 2). The yield ranged between 50–87%.

TABLE-1
PHYSICAL PROPERTIES OF THE LIGANDS AND THEIR COMPLEXES

Sl. No.	Compound	Colour	m.p. (°C)	Yield (%)	% Analysis, Found (Calcd)		
					C	H	N
—	K(Me-dtc)	Pale yellow	151	82.6	16.2 (16.6)	2.3 (2.8)	9.4 (9.7)
—	Na(Chep-dtc)	yellow	95	86.1	45.2 (45.5)	6.4 (6.6)	6.5 (6.6)
—	Na(Chex ₂ -dtc)	yellow	77	72.4	55.6 (55.9)	7.6 (7.9)	5.0 (5.0)
1.	Zn(Me-dtc) ₂ ·CoCl ₂	red-brown	129*	76.9	11.6 (11.8)	1.8 (2.0)	6.9 (6.9)
2.	Zn(Me-dtc) ₂ ·NiCl ₂	brown	112	54.7	11.6 (11.8)	2.0 (2.0)	6.7 (6.9)
3.	Zn(Me-dtc) ₂ ·CuCl ₂	yellow	143*	75.4	11.8 (11.7)	1.9 (1.9)	7.0 (6.8)
4.	[Zn(Me-dtc) ₂ ·CoCl ₂] ₂	olive-green	105	64.9	11.9 (11.8)	1.8 (2.0)	6.7 (6.9)
5.	[Zn(Me-dtc) ₂ ·NiCl ₂] ₂	brown	125	69.2	11.9 (11.8)	2.0 (2.0)	7.0 (6.9)
6.	[Zn(Me-dtc) ₂ ·CuCl ₂] ₂	yellow	143*	86.6	11.7 (11.7)	1.9 (1.9)	6.9 (6.8)
7.	Zn(Chep-dtc) ₂ ·CoCl ₂	olive-green	170	52.3	33.3 (33.6)	5.0 (4.9)	4.7 (4.9)
8.	Zn(Chep-dtc) ₂ ·NiCl ₂	olive-green	210*	66.0	33.7 (33.6)	5.0 (4.9)	4.8 (4.9)
9.	Zn(Chep-dtc) ₂ ·CuCl ₂	blackish	145*	59.1	33.2 (33.4)	5.0 (4.9)	4.7 (4.9)
10.	[Zn(Chep-dtc) ₂ ·NiCl ₂] ₂	green	175*	53.0	33.6 (33.6)	5.0 (4.9)	4.9 (4.9)
11.	[Zn(Chep-dtc) ₂ ·CuCl ₂] ₂	yellow	135*	71.4	33.2 (33.4)	4.9 (4.9)	4.8 (4.9)
12.	Zn(Chex ₂ -dtc) ₂ ·CoCl ₂	green	185*	73.0	44.2 (44.1)	6.2 (6.2)	4.0 (4.0)
13.	Zn(Chex ₂ -dtc) ₂ ·NiCl ₂	green	200*	48.0	44.0 (44.1)	6.2 (6.2)	4.0 (4.0)
14.	Zn(Chex ₂ -dtc) ₂ ·CuCl ₂	pale green	190*	62.2	43.7 (43.8)	6.1 (6.2)	3.8 (3.9)
15.	[Zn(Chex ₂ -dtc) ₂ ·NiCl ₂] ₂	light green	132*	47.4	44.1 (44.1)	6.2 (6.2)	3.8 (4.0)
16.	Zn(Chex ₂ dtc) ₂ ·CuCl ₂] ₂	yellow	146*	58.8	43.7 (43.8)	6.1 (6.2)	3.9 (3.9)

*Compound melts with decomposition

TABLE-2
SELECTED IR BANDS AND MAGNETIC MOMENTS OF THE COMPLEXES

Compound	IR Bands (cm ⁻¹)					μ_{eff} (B.M.)
	$\nu(\text{C—S})$	$\nu(\text{C—N})$	$\nu(\text{Zn—S})$	$\nu(\text{M—S})$	$\nu(\text{M—Cl})$	
K(Me-dtc)	981 w	1456 m	—	—	—	—
Zn(Me-dtc) ₂	962 w	1486 s	360 m	—	—	—
1	982 w, 1001 w	1471 m	353 w	382 w	301 w	4.01
2	982 w, 1009 w	1462 s	390 w	427 w	258 s	0.91
3	982 w, 997 m	1471 w	370 w	386 w	275 w	1.73
4	982 w, 1012 w	1465 w	362 w	393 w	284 w	4.26*
5	979 w, 1011 m	1462 w	366 m	412 w	290 w	3.56*
6	978 m, 1007 w	1471 s	372 m	402 w	256 w, 235 w	1.16*
Na(Chep-dtc)	977 w	1465 s	—	—	—	—
Zn(Chep-dtc) ₂	973 w	1472 s	357 w	—	—	—
7	985 w, 992 w	1485 s	360 w	382 w	290 w	4.39
8	983 w, 1006 w	1461 m	366 m	390 w	286 w	3.90
9	979 w, 1001 w	1456 s	369 w	426 w	305 w	2.20
10	981 w, 1013 m	1460 m	396 w	422 w	292 s	3.55*
11	985 w, 998 m	1456 s	366 w	392 w	251 m	1.91*
Na(CheX ₂ -dtc)	972 w	1461 s	—	—	—	—
Zn(CheX ₂ -dtc) ₂	966 w	1489 m	370 w	—	—	—
12	982 m, 1006 w	1471 s	350 w	391 w	281 m	4.20
13	985 w, 1008 w	1470 m	389 w	420 w	292 w	0.90
14	984 w, 1002 w	1464 s	380 w	409 m	279 m	1.84
15	982 w, 996 w	1468 m	370 w	406 w	270 m	3.68*
16	979 w, 990 w	1465 s	394 w	433 m	297 w	1.77*

*Value is per metal ion

Spectral data and structures

A quick glance to Table-2, one can deduce that the complexes have been formed, especially the significant increase and decrease in the absorption IR bands $\nu(\text{C—S})$ and $\nu(\text{C—N})$, respectively of the precursor complex $\text{Zn}(\text{R-dtc})_2$, on going to its heterobimetallic complexes $[\text{Zn}(\text{R-dtc})_2\text{MCl}_2]_n$, $n = 1$ or 2 . In addition to those, a new band appeared at $430\text{--}380\text{ cm}^{-1}$, which is attributed to $\nu(\text{M—S})$ frequency. These changes in the IR spectra indicate that a coordination of the ligand, dithiocarbamate has been taken place *via* sulfur atoms (Scheme 1).

Cobalt complexes: Cobalt complexes of both types $\text{Zn}(\text{R-dtc})_2\text{CoCl}_2$ and $[\text{Zn}(\text{R-dtc})_2\text{CoCl}_2]_2$, *i.e.*, complexes 1, 7, 12 and 4 respectively showed μ_{eff} values ranged between 4.01–4.39 B.M. (Tables 1 and 2), which all assigned to a tetrahedral configuration. Additional confirmation to this, are the electronic spectral bands appeared at $13000\text{--}18000\text{ cm}^{-1}$ (Table-3), which attributed to the transitions ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P}) (\nu_3)$ and the appearance of many bands in this region is attributed to the distortion in the tetrahedral configuration.^{18, 19}

TABLE-3
ELECTRONIC SPECTRA AND MOLAR CONDUCTIVITY OF THE COMPLEXES
(IN CH₃CH)

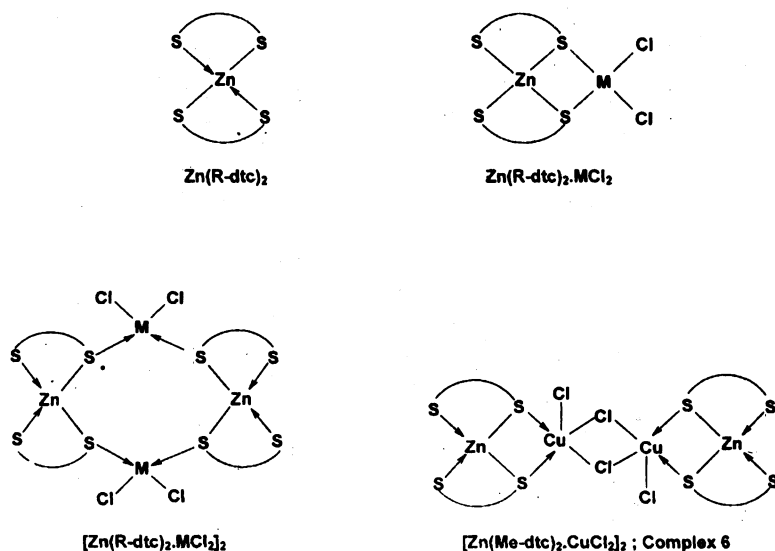
Complex Seq.	Spectra (cm ⁻¹)	Λ_M mol ⁻¹ cm ² ohm ⁻¹
1.	14010, 14860, 15530, 16200, 17990	42.3
2.	9740, 15380, 16820, 21140, 30580	28.3
3.	15380, 24330, 30670	38.6
4.	14670, 15480, 16070, 18100	19.9
5.	9810, 15120, 16010, 29900, 31200	21.5
6.	12820, 13560, 15400, 16010, 23100	30.3
7.	13820, 14740, 15380, 16120, 18010, 32010	19.9
8.	9780, 15625, 16010, 29230	35.5
9.	15130, 25460, 37040	19.9
10.	9830, 14730, 15830, 31020	15.6
11.	9340, 24960, 32820	19.9
12.	13980, 14820, 16010, 16950, 18100	41.5
13.	9730, 14940, 15780, 20980, 31020	35.1
14.	17010, 33340	40.2
15.	9810, 9940, 15480, 16100, 32200	32.6
16.	9700, 24050, 32080	18.3

Nickel complexes: The nickel complexes 5, 8, 10 and 16 (Table-1) showed μ_{eff} values ranged between 3.55–3.99 B.M. (Table-2) assigned to tetrahedral configurations. Also the electronic spectra consist of two fundamental bands, the first one at 9800 cm⁻¹, while the second one being splitted into two bands at 14700 and 16000 cm⁻¹. The latter is attributed to the two transitions $^3T_1(F) \rightarrow ^3A_2(F) (\nu_2)$ and $^3T_1(F) \rightarrow ^3T_1(P) (\nu_3)$, respectively, in the distorted tetrahedral configuration due to the splitting occurred in the band ν_3 ²⁰. On the contrary, the nickel complexes 2 and 13 showed magnetic values of *ca.* 0.9 B.M. which could be due to the presence of both the tetrahedral and the square planer configurations with a lower proportion of the latter (not exceeding 30%)²¹. Further confirmation to that are the electronic spectra which assigned to the presence of a mixture of both configurations, the tetrahedral and the square planer, in which the bands at *ca.* 9700 and 15000–16000 cm⁻¹ are attributed to the tetrahedral one (as in the complexes 5, 8, 10 and 15 above). The spectral band appeared at *ca.* 21000 cm⁻¹ is attributed to the square planer configuration; the transition $^1A_{1g} \rightarrow ^1B_{1g}$, whereas the second band for the tetrahedral, *i.e.*, 15000–16000 cm⁻¹ could be also attributed to the square planer; the transition $^1A_{1g} \rightarrow ^1A_{2g}$.

Copper complexes: Apart of complex 6, all copper complexes 3, 9, 11, 14 and 16 (Tables 1 and 2) gave magnetic properties with μ_{eff} ranging between 1.7–2.2 B.M. which are normal for copper(II) complexes with some orbital

contributions. In contrast, complex 6 showed μ_{eff} of 1.16 B.M. indicating that antiferromagnetic interaction occurred, and this is possible when more than one ion bridged by a ligand. The electronic spectra of complexes 3 and 11 (Table-3) indicate that copper(II) ion arranged in a tetrahedral structure since their spectra showed two bands at 9340 and 9700 cm^{-1} and none existed in the region 10000–20000 cm^{-1} . On the contrary, the electronic spectra of complexes 3, 9 and 14 showed bands in the region 15000–17000 cm^{-1} which are certainly indicating the square planer configuration. The spectrum of complex 14, as a unique case, showed multiple bands in the region 12820–16010 cm^{-1} . These band values are inconsistent, neither with those of square planer nor with those of octahedral configurations, but similar to those of penta-coordinate copper(II) complexes.^{22, 23} Further support to this argument is the presence of a new additional IR absorption band at 235 cm^{-1} which attributed to $\nu(\text{Cu}-\text{Cl})$ for bridging chlorine in the complex. Thus we could safely propose a structure of complex 6 as it compiled in Scheme 1.²⁴

Conductivity measurements: All the complexes prepared in this work showed conductivity values ranged between 18–24 $\text{mol}^{-1} \text{cm}^2 \text{ohm}^{-1}$ (Table-3) in acetonitrile at ambient temperature, indicating non-conductive species, since 1 : 1 conductive species should give conductivity ranging between 120–160 $\text{mol}^{-1} \text{cm}^2 \text{ohm}^{-1}$ in the same solvent.²⁵



Scheme 1. The suggested structures of the complexes studied in the present work

REFERENCES

1. H. Shimada, N. Sugimachi, T. Funakoshi and S. Kojima, *Toxicol Lett.*, **66**, 193 (1993), S. Hidaka, M. Tsuruoka, T. Funakoshi, H. Shimada, M. Kiyozumi and S. Kojima, *Ren. Fail.*, **16**, 337 (1994).
2. J. Kaur, S.S. Marwaha and G.S. Sodhi, *J. Indian Chem. Soc.*, **76**, 185 (1999), H. Singh, V.K. Srivastava, S.N. Shukla and M.K. Upadhyaya, *Indian J. Chem.*, **31A**, 472 (1992).
3. P.C. Andrews, S.M. Lawrence, C.L. Raston, B.W. Skelton, V.A. Tolhurst and A.H. White, *Inorg. Chim. Acta*, **300-302**, 56 (2000).
4. J. Sharma, Y. Singh and A.K. Rai, *Phosph. Sulf. Silic. Rela. Elem.*, **112**, 19 (1996).
5. G. Hogarth, A. Pateman and S.P. Redmond, *Inorg. Chim. Acta*, **306**, 232 (2000).
6. M. Sokolov, H. Imoto and T. Saito, *Inorg. Chem. Commun.*, **2**, 422 (1999).
7. G. Exarchos, S.D. Robinson and J.W. Steed, *Polyhedron*, **19**, 1511 (2000).
8. K. Oyaizu, K. Yamamoto, Y. Ishii and E. Tsuchida, *Chem. Europ. J.*, **5**, 3193 (1999).
9. M.V. Galakhov, P. Gomez-Sal, T. Pedraz, M.A. Pellinghelli, P. Royo, A. Tiripicchio and A.V. de Miguel, *J. Organometal. Chem.*, **579**, 190 (1999).
10. F. Demaimay, A. Roucoux, N. Noiret and H. Patin, *J. Organometal. Chem.*, **575**, 145 (1999).
11. T.A.K. Al-Allaf, I.A. Mustafa and S.E. Al-Mukhtar, *Transition Met. Chem.*, **18**, 1 (1993).
12. T.A.K. Al-Allaf, N.H. Buttrus and H.R. Yousif, *Asian J. Chem.*, **12**, 527 (2000).
13. T.A.K. Al-Allaf, M.J. Mohammed and S.E. Al-Mukhtar, *Mutah J. Res. Stud. (Jordan)*, **10**, 67 (1995).
14. T.A.K. Al-Allaf, M.J. Mohammed and I.A. Mustafa, *Iraqi. J. Chem.*, **25**, 170 (1999).
15. L.J. Rshan, M.J. Mohammed, A.A. Aziz, T.A.K. Al-Allaf and K.D. Sulayman, *Boll. Chim. Farm. (Italy)*, **133**, 662 (1994), L.J. Rshan., T.A.K. Al-Allaf and R.F. Khuzaie, *Boll. Chim. Farm. (Italy)*, **134**, 464 (1995).
16. G.A. Brewer, R.J. Butcher, B. Letafat and E.K.K. Sinn, *Inorg. Chem.*, **22**, 371, (1981), and references therein.
17. W.U. Malik, R. Bembi and V.K. Bhardwaj, *J. Indian Chem. Soc.*, **57**, 36 (1980).
18. L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 277 (1964).
19. C.M. Mikuliski, S. Grossaman, M.L. Bayne, M. Gaul, D.L. Staley and A. Renn, *Inorg. Chim. Acta*, **161**, 29 (1989).
20. S. Buffagni, L.M. Vallavino and J.V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).
21. B.S. Manhas, S. Bala, R. Tagannathan and A.S. Dindsa, *Indian J. Chem.*, **28A**, 258 (1989)
22. M. Akbar Ali, S.K. Livingstone and D.J. Phillips, *Inorg. Chim. Acta*, **7**, 531 (1973).
23. L. El-Sayed, M.F. Iskander and A.E. Al-Toukhy, *J. Inorg. Nucl. Chem.*, **36**, 1739 (1974).
24. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 3rd Edn., Wiley, p. 339 (1978).
25. F.A. Kettle, *Coordination Compounds*, Thomas Nelson & Sons. p. 168 (1975).