

NEW TRANSITION METAL OXALATO COMPLEXES WITH DABCOH₂²⁺ AS ADVERSE CATION: SYNTHESIS AND INFRARED STUDY

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Abstract: On allowing DABCOH₂(HC₂O₄)₂ to react with transition metal dihalides in ethanol, a new series of complexes of general formula M(oxalate)₂ DABCOH₂²⁺. nDABCOH₂²⁺.2X⁻ (n=1/2;1) have been obtained. When (n=1) a dimeric structure is suggested, the two monomeric species being hold together by biprotonated DABCO through N-H...O hydrogen bonds. In the case of the complex M(oxalate)₂DABCOH₂²⁺.1/2 DABCOH₂²⁺.2X⁻ -M = Ni, Cu- the structure is an infinite chain. The environment around the metallic centers is octahedral or square pyramidal. The oxalate behaves as a monochelating and hydrogen bonds involved ligand or is only concerned by hydrogen bonds.

Keywords: fullerene, dimeric or infinite chain structures, hydrogen bonds, monochelating ligand, octahedral or square planar environments

1. INTRODUCTION

The acidic substituted ammonium salts, because of their solubility in organic solvents have been used by several groups to reach new complexes of metals, transitional or not [1-5]. In this dynamic focusing in oxalic acid salts, our group has yet reported several papers in this field [6-8]. Rao et al. [9] have reported the crystal structure of DABCOH₂(HC₂O₄)₂. We initiate here the study of the interactions between Rao et al. salt [9] and some transitional metal halides which has yielded ten new complexes containing the core DABCOH₂(C₂O₄).MC₂O₄.nDABCOH₂.2X⁻ (X = Cl, Br) (n=1/2;1) whose infrared study have been carried out then structures suggested on the basis of infrared data.

2. MATERIALS AND METHODS

We have obtained Rao et al. salt [9] – DABCOH₂(HC₂O₄)₂ – (L) on mixing DABCO and oxalic acid in ethanol in 1/2 ratio after a slow solvent evaporation.

The studied adducts have been obtained on mixing – DABCOH₂(HC₂O₄)₂ – (L) with CoCl₂.6H₂O, CuBr₂, NiCl₂.6H₂O and CuCl₂.2H₂O in various ratios in ethanol. All the mixtures give a clear solution; a powder is obtained after a slow solvent evaporation. The following compounds were obtained for specific ratios -(L)/metal halide-:

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- **L** ($4,2 \cdot 10^{-4}$ mol) + **CoCl₂.6H₂O** ($9,67 \cdot 10^{-5}$ mol) in 2/1 ratio gives **(A)** as a yellow powder with a yield of 19.70 %;
- **L** ($4,2 \cdot 10^{-4}$ mol) + **CuBr₂** ($9,58 \cdot 10^{-5}$ mol) in 2/1 ratio gives **(B)** as a yellow powder with a yield of 22.5 %;
- **L** ($4,2 \cdot 10^{-4}$ mol) + **NiCl₂.6H₂O** ($1,26 \cdot 10^{-4}$ mol) in 2/1 ratio gives **(C)** as a yellow powder with a yield of 36.25 %;
- **L** ($4,2 \cdot 10^{-4}$ mol) + **CuCl₂** ($1,58 \cdot 10^{-4}$ mol) in 2/1 ratio gives **(D)** as a yellow powder with a yield of 36.25 %;
- **L** ($4,2 \cdot 10^{-4}$ mol) + **CoCl₂.6H₂O** ($1,26 \cdot 10^{-4}$ mol) in 2/1 ratio gives **(E)** as a beige powder with a yield of 24.17 %;
- **L** ($4,2 \cdot 10^{-4}$ mol) + **CuBr₂** ($5,06 \cdot 10^{-4}$ mol) in 1/2 ratio gives **(F)** as a yellow powder with a yield of 12.05 %;
- **L** ($4,2 \cdot 10^{-4}$ mol) + **CuBr₂** ($1,26 \cdot 10^{-4}$ mol) in 2/1 ratio gives **(G)** as a yellow powder with a yield of 14.29 %;
- **L** ($4,2 \cdot 10^{-4}$ mol) + **NiCl₂.6H₂O** ($3,83 \cdot 10^{-4}$ mol) in 1/2 ratio gives **(H)** as a yellow powder with a yield of 11,57 %;
- **L** ($4,2 \cdot 10^{-4}$ mol) + **NiCl₂.6H₂O** ($4,63 \cdot 10^{-5}$ mol) in 2/1 ratio gives **(I)** as a yellow powder with a yield of 50 %;
- **L** ($4,2 \cdot 10^{-4}$ mol) + **CuBr₂** ($1,93 \cdot 10^{-4}$ mol) in 2/1 ratio gives **(J)** as a yellow powder with a yield of 12.38 %.

The analytical data reported below have allowed suggesting the following formulae for the ten new complexes (Table 1).

Table 1. Chemical composition of suggested compounds.

Compound	Suggested compounds	Chemical composition [% mass]					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
(A)	DABCOH ₂ C ₂ O ₄ .CoC ₂ O ₄ .DABCOH ₂ Cl ₂ .2EtOH.3H ₂ O	35.96	35.96	5.24	5.32	10.49	10.41
(B)	DABCOH ₂ C ₂ O ₄ .CuC ₂ O ₄ .DABCOH ₂ Br ₂ .4EtOH.1/2 DABCO	37.36	37.34	6.69	6.61	8.07	8.03
(C)	DABCOH ₂ C ₂ O ₄ .NiC ₂ O ₄ .DABCOH ₂ Cl ₂ .1/2DABCO.H ₂ O	39.25	38.91	6.93	6.95	13.47	13.37
(D)	[DABCOH ₂]C ₂ O ₄ .CuC ₂ O ₄ .2[DABCOH ₂ Cl ₂].2H ₂ O	34.76	35.02	6.07	6.06	11.06	11.14
(E)	3[DABCOH ₂]C ₂ O ₄ .CoC ₂ O ₄ .[DABCOH ₂ Cl ₂]	44.10	44.26	7.35	7.59	14.70	14.23
(F)	2[DABCOH ₂]C ₂ O ₄ .CuC ₂ O ₄ .2[DABCOH ₂ Br ₂]	44.10	43.78	7.35	7.49	14.7	14.61
(G)	DABCOH ₂ C ₂ O ₄ .CuC ₂ O ₄ .DABCOH ₂ Cl ₂ .DABCO.H ₂ O	39.49	39.33	6.28	6.33	12.5	12.34
(H)	DABCOH ₂ C ₂ O ₄ .NiC ₂ O ₄ .DABCOH ₂ Cl ₂ .1/2H ₂ O	37.59	37.43	6.26	6.33	9.74	9.68
(I)	DABCOH ₂ C ₂ O ₄ .Ni(C ₂ O ₄).1/2[DABCOH ₂ Cl ₂]	35.36	35.49	4.98	4.95	9.52	9.44
(J)	DABCOH ₂ C ₂ O ₄ .CuC ₂ O ₄ .1/2[DABCOH ₂ Cl ₂].EtOH	34.12	34.22	5.12	5.16	7.96	8.06

Elemental analyses and IR spectra (performed on a Bruker FT-IR spectrometer) have been obtained from Rhodes University of Grahamstown-South Africa.

IR abbreviations: br (broad) vs (very strong); s (strong); m (medium). Chemical reagents are purchased from ALDRICH Company (Germany) and used as received.

3. RESULTS AND DISCUSSION

Let us consider the infrared data of complexes **(A)**, **(B)**, **(C)**, **(D)**, **(E)**, **(F)**, **(G)**, **(H)**, **(I)** and **(J)** in cm⁻¹:

- (A)**: $\nu_{as}(\text{CO}_2)$ 1670(vs), $\nu_s(\text{CO}_2)$ 1281(s), $\delta(\text{CO}_2)$ 780(s), $\nu_{as}(\text{H}_2\text{O})$ 3350(br), ($\nu_{OH} + \nu_{NH}$) 2880(br);
(B): $\nu_{as}(\text{CO}_2)$ 1692.84(vs), $\nu_s(\text{CO}_2)$ 1285.88(m), $\delta(\text{CO}_2)$ 781.93(m), ($\nu_{OH} + \nu_{NH}$) 3521.18(br), 3035.8(br);
(C): $\nu_{as}(\text{CO}_2)$ 1691.93(vs), $\nu_s(\text{CO}_2)$ 1323.10(m), $\delta(\text{CO}_2)$ 772.04(m), $\nu_{as}(\text{H}_2\text{O})$ 3519.64(br), (ν_{NH}) 3479.36(br), 2986.21(br);
(D): $\nu_{as}(\text{CO}_2)$ 1618.74(vs), $\nu_s(\text{CO}_2)$ 1311.09(m), $\delta(\text{CO}_2)$ 794.77(m), $\nu_{as}(\text{H}_2\text{O})$ 3369.04(br), (ν_{NH}) 2977.94(br);
(E): $\nu_{as}(\text{CO}_2)$ 1618.40(s), $\nu_s(\text{CO}_2)$ 1233.84(m), $\delta(\text{CO}_2)$ 793.99(m), (ν_{NH}) 3367.16(br), 2921.71(br);
(F): $\nu_{as}(\text{CO}_2)$ 1623(m), $\nu_s(\text{CO}_2)$ 1372.56(s), $\delta(\text{CO}_2)$ 797.87(s), (ν_{NH}) 3362.74(br), 2920.07(br);

(G): $\nu_{\text{as}}(\text{CO}_2)$ 1615.04(vs), $\nu_{\text{s}}(\text{CO}_2)$ 1308.54(m), $\delta(\text{CO}_2)$ 761.15(m), $\nu_{\text{as}}(\text{H}_2\text{O})$ 3415.32(br), (ν_{NH}) 3014.33(br);
 (H): $\nu_{\text{as}}(\text{CO}_2)$ 1692.56(s), $\nu_{\text{s}}(\text{CO}_2)$ 1325.08(m), $\delta(\text{CO}_2)$ 805.15(m), $\nu_{\text{as}}(\text{H}_2\text{O})$ 3525.45(br), (ν_{NH}) 3448.93(br), 2850.17(br);

(I): $\nu_{\text{as}}(\text{CO}_2)$ 1678(vs), $\nu_{\text{s}}(\text{CO}_2)$ 1297.8(s), $\delta(\text{CO}_2)$ 782.5(vs), (ν_{NH}) 2975(br);

(J): $\nu_{\text{as}}(\text{CO}_2)$ 1693.07(vs), $\nu_{\text{s}}(\text{CO}_2)$ 1322.88(m), $\delta(\text{CO}_2)$ 783.14(m), ($\nu_{\text{OH}}+\nu_{\text{NH}}$) 3450.93(br), 3034.96(br).

The adducts (A), (H), (B), (G) and (C) are only different by the lattice molecules involved, so we will chose the first compound as the parent molecule. The suggested structure is a dimer with a CoCl_2 surrounded by two monochelating oxalates, the environment around the metallic centre being octahedral, the two cores being connected *via* N-H...O hydrogen bonds by the biprotonated DABCO. The water and ethanol molecules are lattice (Figure 1).

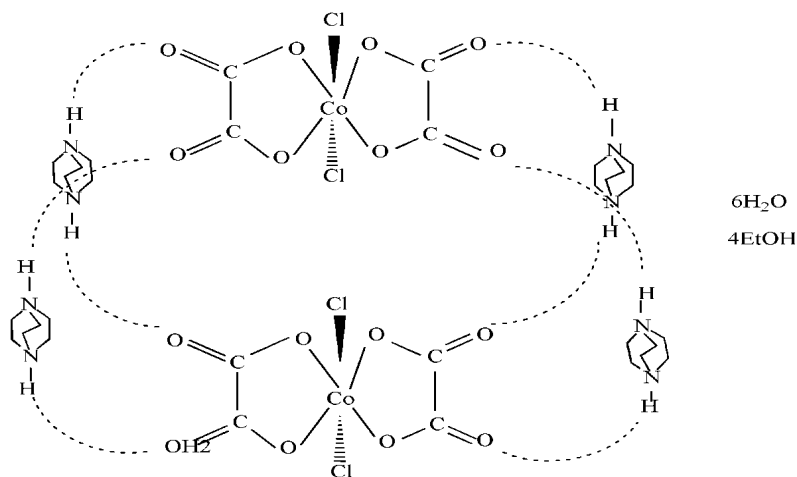


Fig. 1. Proposed structure for (A).

NB These other complexes are only different through the number of lattice molecules (EtOH, DABCO, H_2O) involved. The suggested structure for (B) is similar to the one of (A), the chlorido atoms being replaced by bromido ones, the ethanol and the DABCO molecules being lattice.

For the complex (D) we can maintain the dimeric nature of the above complexes but in this case the string connecting the two complex –anions is $\text{DABCOH}_2^{2+}\dots\dots\text{Cl}^-\dots\dots\text{DABCOH}_2^{2+}$ rather than one DABCOH_2^{2+} . The two chloride atoms involved in the strings are then connected by another $\text{DABCOH}_2^{2+}\dots\dots\text{Cl}^-\dots\dots\text{DABCOH}_2^{2+}$ string, the remaining chloride atom being involved in electrostatic interactions with the main component of the structure. The hydrogen bonds between the biprotonated DABCO and the oxalates are bifurcated ones (Figure 2).

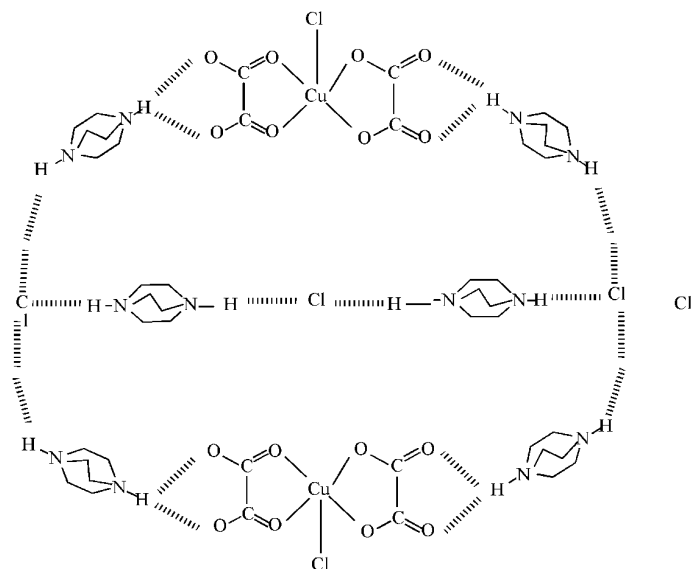
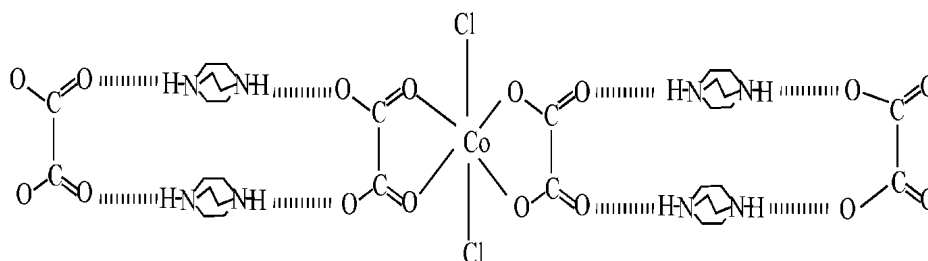


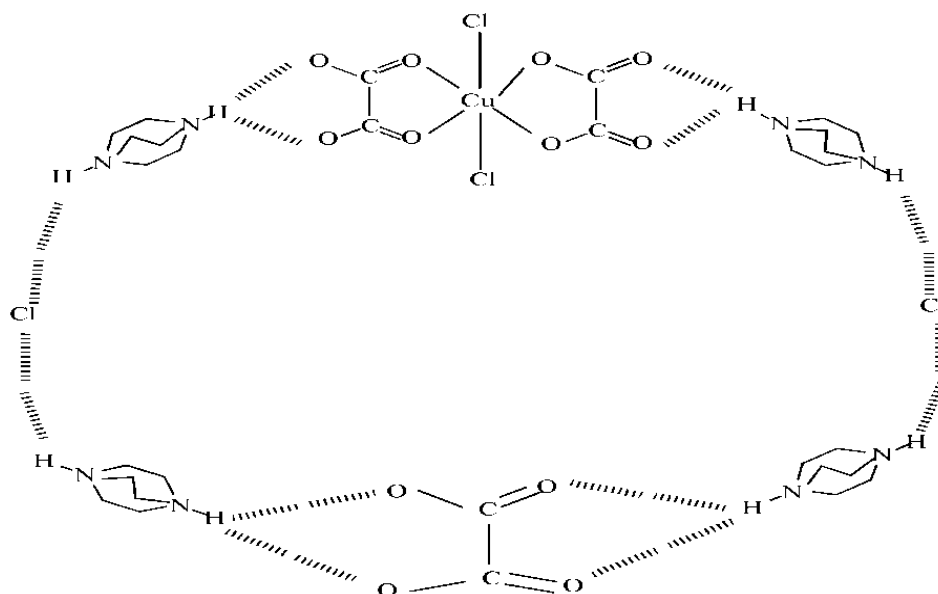
Fig. 2. Proposed structure for (D).

(E) $3[\text{DABCOH}_2]\text{C}_2\text{O}_4 \cdot \text{CoC}_2\text{O}_4 \cdot [\text{DABCOH}_2\text{Cl}_2]$

This compound is **(A)** to which has been added two molecules of $\text{DABCOH}_2\text{C}_2\text{O}_4$ the suggested structure is a monomer consisting of a $[\text{CoCl}_2(\text{C}_2\text{O}_4)]^{2-}$ core as in **(A)** to which are connected in both sides $[(\text{DABCOH}_2)_2\text{C}_2\text{O}_4]^{2+}$; the structure is reported in Figure 3.

Fig. 3. Proposed structure for **(E)**.**(F)** $2[\text{DABCOH}_2]\text{C}_2\text{O}_4 \cdot \text{CuC}_2\text{O}_4 \cdot 2[\text{DABCOH}_2\text{Cl}_2]$

This complex of copper contains the core $[\text{CuCl}_2(\text{C}_2\text{O}_4)_2]^{4-}$ and a long $\text{DABCOH}_2^{2+} \dots \text{Cl}^- \dots \text{DABCOH}_2^{2+} \dots \text{oxalate} \dots \text{DABCOH}_2^{2+} \dots \text{Cl}^- \dots \text{DABCOH}_2^{2+}$ connecting through bifurcated N-H...O,O hydrogen bonds the two monochelating oxalates (Figure 4).

Fig. 4. Proposed structure for **(F)**.**(I)** $\text{DABCOH}_2\text{C}_2\text{O}_4 \cdot \text{Ni}(\text{C}_2\text{O}_4) \cdot 1/2[\text{DABCOH}_2\text{Cl}_2]$,**(J)** $\text{DABCOH}_2\text{C}_2\text{O}_4 \cdot \text{CuC}_2\text{O}_4 \cdot 1/2[\text{DABCOH}_2\text{Cl}_2] \cdot \text{EtOH}$

The structure of the complex **(I)** is also dimeric, the core being $[\text{NiCl}(\text{C}_2\text{O}_4)_2]^{3-}$ (the environment around the metallic centre is a square based pyramid), the biprotonated DABCO connecting through bifurcated N-H...O,O hydrogen bonds the oxalates of each core but also the chlorido atoms through N-H...Cl leading to an infinite chain structure reported in Figure 5. For **(J)** a lattice molecule of ethanol is added to the **(I)** structure.

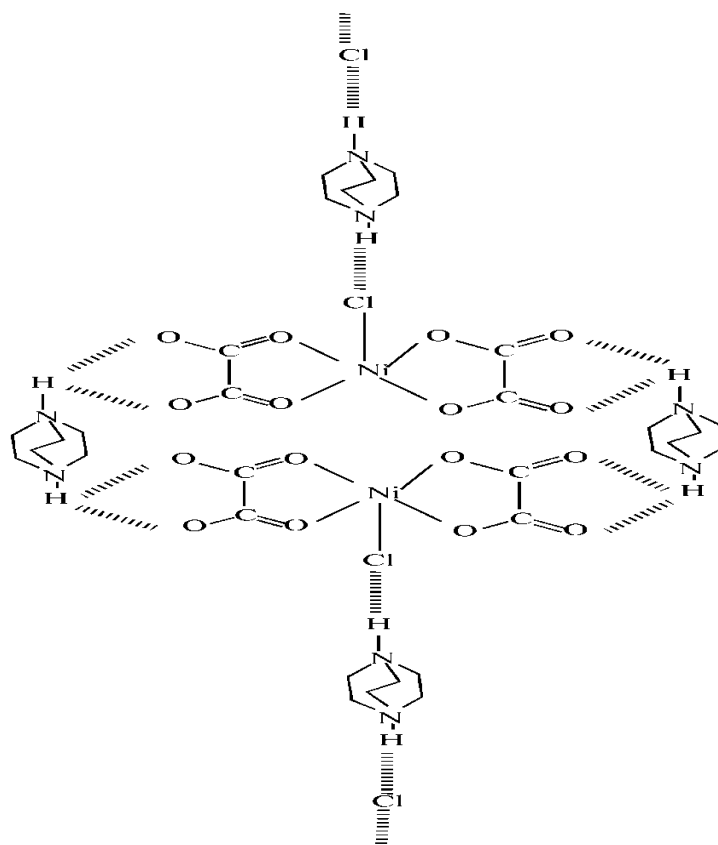


Fig. 5. Proposed structure for (I).

4. CONCLUSIONS

The studied complexes have dimeric -or infinite chain- structures, the environments being octahedral or square based pyramidal, the oxalate behaving as a monochelating and bifurcated hydrogen bonds involved ligand or only bifurcated hydrogen bonds concerned. Biprotonated DABCO alone or biprotonated DABCO, chlorido atoms and oxalate anion strings are involved in all the structures connecting oxalates or chloride and bromido atoms.

ACKNOWLEDGEMENTS

We deeply thank Professor Tebello Nyokong from Rhodes University, Grahamstown, South Africa, for her equipment support.

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