

# Dinuclear Complexes of Diethyl 2-(2-Carboxyphenylhydrazono)-3-oxopentanedioate with some Transition Metal Ions

*J. Chem. Research (S),*  
1998, 16–17  
*J. Chem. Research (M),*  
1998, 0201–0213

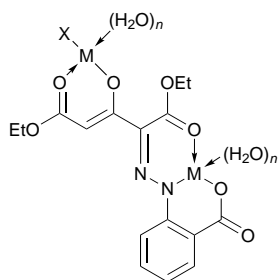
Yousry M. Issa,\* Nour T. Abdel-Ghani and Maha F. Abo El-Ghar

*Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt*

Manganese(II), cobalt(II), copper(II), zinc(II), cadmium(II) and mercury(II) complexes of diethyl 2-(2-carboxyphenylhydrazono)-3-oxopentanedioate have been prepared and characterized by IR, <sup>1</sup>H NMR and UV spectroscopy, magnetic moment measurements and thermogravimetric analysis.

Coordination compounds with several dinucleating ligands have been studied as models for naturally occurring systems<sup>1</sup> and in the domain of metallo-enzymes and homogeneous catalysis. The synthesis of dinuclear complexes involves choice of a suitable ligand which can coordinate through more than one chelation centre.<sup>5</sup> Diethyl 3-oxopentanedioate can be regarded as a precursor for 2-arylhydrazone derivatives having two separate centres of chelation. This article deals with the synthesis and structural characterization of diethyl 2-(2-carboxyphenylhydrazono)-3-oxopentanedioate (H<sub>2</sub>L) complexes with some divalent metal ions, Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Hg<sup>II</sup>. The ligand acts as a β-oxo ester and an α-oxo 2-carboxyphenylhydrazone: it may chelate to two metal ions *via* the enolic OH and CO (unconjugated ester) on one side, and the NH, CO (conjugated ester) and OH (carboxylic) on the other side.

Diethyl 2-(2-carboxyphenylhydrazono)-3-oxopentanedioate was prepared according to the method described in the literature.<sup>14</sup> The complexes were prepared by mixing 1 mol equiv. of the ligand with 2 mol equiv. of the metal chloride in ethanol and boiling for 10 min. NaOH (3 mol equiv.) was then added gradually with continuous stirring while boiling. The mixture was diluted with distilled water and the product was collected by filtration and washed several times with ethanol till the filtrate was colourless. The complexes, M<sub>2</sub>LCl·nH<sub>2</sub>O [M = Mn<sup>II</sup>, Co<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>; n = 2–6] and Ni<sub>2</sub>L·OH·6H<sub>2</sub>O, were isolated in 60–65% yield. The structure of the dinuclear complexes may be proposed as:



M	n	X
Mn, Cu, Zn, Cd, Hg	1	Cl
Co	3	Cl
Ni	3	OH

The IR spectra of the M<sup>II</sup>-H<sub>2</sub>L complexes showed masking of the ν<sub>NH</sub> of the hydrazo group and ν<sub>OH</sub> of the carboxylic group attached to the aromatic moiety by a very broad band centred at *ca.* 3400 cm<sup>-1</sup> which can be assigned to ν<sub>OH</sub> of the water molecules coordinated to the metal ion. New bands at 1275–1264 cm<sup>-1</sup> corresponding to a δ<sub>OH</sub>(H<sub>2</sub>O) deformation and at 690 cm<sup>-1</sup> assigned to a H<sub>2</sub>O rocking vibration<sup>17</sup> were observed. ν<sub>C=O</sub> appeared as a medium-intensity band at 1732–1676 cm<sup>-1</sup> which could be taken as evidence for the

participation of C=O groups in chelation. The CH bending vibration band of the —CH<sub>2</sub>—CO— moiety at 1420 cm<sup>-1</sup> disappeared on chelation, indicating its involvement in the coordination through the enolic form of the ligand. The appearance of a new band at 1610, 1611 and 1613 cm<sup>-1</sup> for the Co<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup> complexes, respectively, emphasized the presence of C=C as a result of enolization. New bands observed at 468–428 and 406–416 cm<sup>-1</sup> were assigned to ν<sub>M—N</sub><sup>19</sup> and ν<sub>M—O</sub><sup>20</sup> respectively.

The <sup>1</sup>H NMR spectrum of the ligand showed two adjacent triplets at δ 1.20 and 1.30, and two quartets at δ 4.10 and 4.35 corresponding to the six protons (two CH<sub>3</sub>) and four protons (two CH<sub>2</sub>) of the two ethyl groups, respectively. A singlet was observed at δ 3.95 corresponding to the active methylene group.<sup>21</sup> The aromatic protons were shown as multiplet signals at δ 7.25, 7.75, 7.90 and 8.05. The NH and CO<sub>2</sub>H protons showed signals at δ 13.89 and δ 3.40, respectively, which disappeared on deuteration. [Cd<sub>2</sub>LCl·2H<sub>2</sub>O] and [Hg<sub>2</sub>LCl·2H<sub>2</sub>O] showed disappearance of the NH proton, indicating the involvement of the NH in chelation. Disappearance of the active methylene protons as well as the appearance of a new singlet at δ 7.0 corresponding to the methine proton (=CH) indicated enolization of the oxo group as a result of chelation. The participation of the CO<sub>2</sub>H proton in chelation cannot be accounted for from the <sup>1</sup>H NMR spectra because of the water peak that appeared as a strong sharp singlet at the same position (δ 3.5).

Thermogravimetric analysis curves showed no mass loss below 150 °C, indicating absence of water of hydration in the complexes. Removal of coordinated water molecules started at about 200 °C. This was supported by the appearance of an endothermic peak in the DTA curves over the same temperature range. The decomposition of the Mn<sup>II</sup>, Co<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> complexes proceeded as a one-step combustion, associated by an exothermic peak in the DTA curve, at 330–490 °C, leading to a final product as MnO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, CuO or ZnO associated with their corresponding metal chlorides. The final residue of the Ni<sup>II</sup> complex amounted to 28%, indicating the formation of NiO. The data were in conformity with the metal content obtained from EDTA titration.

The electronic absorption band of [Mn<sub>2</sub>LCl·2H<sub>2</sub>O] at 27 144 cm<sup>-1</sup> suggested a tetrahedral structure and the value of the magnetic moment μ<sub>eff</sub> (5.21 μ<sub>B</sub> per metal ion) was as expected for a high-spin 3d<sup>5</sup> system.<sup>22</sup> Bands at 17 500 and 26 247 cm<sup>-1</sup> for [Co<sub>2</sub>LCl·6H<sub>2</sub>O] and [Ni<sub>2</sub>L·OH·6H<sub>2</sub>O] assigned to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) transitions, respectively, reflected the octahedral geometry around the Co<sup>II</sup> and Ni<sup>II</sup> metal ions, while the values of μ<sub>eff</sub> (3.97 μ<sub>B</sub> and 3.00 μ<sub>B</sub> per metal ion, respectively) were typical of those reported for high-spin Co<sup>II</sup> ions<sup>23</sup> and were in the same range as reported for octahedral geometry around Ni<sup>II</sup> ions.<sup>24</sup> The magnetic moment of [Cu<sub>2</sub>LCl·2H<sub>2</sub>O] was 1.64 μ<sub>B</sub> per metal ion, a lower value than that normally reported for an unpaired electron in the Cu<sup>II</sup> metal ion and which may be attributed to a spin-exchange interaction between the two Cu<sup>II</sup> ions.<sup>25</sup> The electronic spectrum showed a band at 24 746

\*To receive any correspondence.

$\text{cm}^{-1}$  assigned to a ligand–metal charge transfer, probably a  $\pi-\pi^*$  transition.<sup>26</sup>  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  ions were diamagnetic in their complexes.

Techniques used: IR,  $^1\text{H}$  NMR, UV, magnetic moment measurements, TG

References: 26

Tables: 4 (formula, elemental analyses, magnetic moment, UV, IR,  $^1\text{H}$ -NMR and TG)

Received, 27th May 1997; Accepted, 19th September 1997  
Paper E/7/03623J

#### References cited in this synopsis

- 1 K. Takahashi, Y. Nishida, Y. Maeda and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1985, 2375.
- 2 M. Tanaka, M. Kitaoka, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2469.
- 3 (a) C. Bülow and W. Hopfner, *Ber. Dtsch. Chem. Ges.*, 1901, **34**, 71; (b) C. Bülow and H. Goller, *Ber. Dtsch. Chem. Ges.*, 1911, **44**, 2835.
- 4 R. C. Mishra, B. K. Mahapatra and D. Panda, *J. Indian Chem. Soc.*, 1983, **58**, 80.
- 5 E. P. Powell and N. Sheppard, *Spectrochim. Acta*, 1961, **17**, 68.
- 6 C. Djordjevic, *Spectrochim. Acta*, 1961, **17**, 448.
- 7 B. P. Dailey and J. W. Shoolery, *J. Am. Chem. Soc.*, 1955, **77**, 3977.
- 8 D. H. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 1961, 3735.
- 9 A. T. Casey and S. Mitra, in *Theory and Application of Molecular Paramagnetism*, ed. E. A. Boudreaux and I. N. Mulay, Wiley, New York, 1976.
- 10 G. M. Abou El-Reash, *Synth. React. Inorg. Met.-Org. Chem.*, 1993, **23**, 825.
- 11 H. C. Rai and B. N. Sharma, *Asian J. Chem.*, 1995, **7**, 775.
- 12 A. K. Gregson, R. L. Martin and S. Mitra, *Proc. R. Soc. London, Ser. A*, 1971, **320**, 473.