

Reactivity of Some Transition Metal Complexes of Anthranilic Acid with Leucine and Monochloroacetic Acid

A. M. El-Roudi^a, A. A. M. Aly^b, A. A. Abd El-Gaber^a, and M. El-Shabasy^c

^a Chemistry Department, Faculty of Science, Minia University, Minia, Egypt.

^b Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt.

^c Physics Department, Faculty of Science, Minia University, Minia, Egypt.

Received June 4, 1987

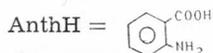
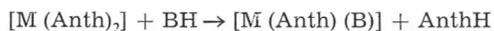
Six mixed ligand complexes of $[M(\text{Anth})(\text{Leu}) \cdot n\text{H}_2\text{O}]$ and $[M(\text{Anth})(\text{Clac})]$ types, where $M = \text{Co}, \text{Ni}$ and Cu ; $n = 0, 2$ or 4 ; Anth = anthranilate and Leu = leucinate, have been prepared. They were characterized on the basis of their analyses, infrared and UV-VIS spectra, magnetic and thermal measurements. All the compounds were found to have presumably distorted octahedral configurations. The polymeric structure of the complexes is indicated by their insolubility and high thermal stability.

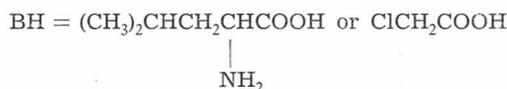
INTRODUCTION

There have been several studies¹⁻⁵ concerned with transition metal complexes of anthranilic acid. Only brief attention has been directed to mixed ligand complexes of this acid or its derivatives.⁶⁻⁸ In view of our interest in mixed ligand complexes⁹⁻¹¹ and also in view of the fact that mixed ligand complexes play an important role in many naturally occurring biological processes¹², we undertook a study of the synthesis and characterization of some transition metal mixed ligand complexes of anthranilic acid with leucine and monochloroacetic acid. The latter acid was of interest because haloacetate ions are known to form a great number of complexes with transition metal ions giving rise to different coordination numbers and stereochemistries; they can act as monodentate, chelating or bridging acetate groups.¹³⁻¹⁵

RESULTS AND DISCUSSION

The complexes were obtained readily from the reaction of anthranilic acid complexes with leucine or monochloroacetic acid according to the following equation:





The complexes are insoluble in common organic solvents; they are only fairly soluble in dimethylsulphoxide, which may be an indicative evidence of their polymeric structures. Their analytical data, colour and magnetic moment are tabulated in Table I.

TABLE I
Analytical Data and Physical Properties of the Complexes

Compound	Colour	Analytical data [%/0] ^a			μ_{eff} (B. M.)
		C	H	Cl	
[Co(Anth)(Leu)] · 4H ₂ O	pink	39.1 (39.3)	6.3 (6.5)	—	3.83
[Ni(Anth)(Leu)]	pale green	47.8 (48.0)	5.4 (5.5)	—	3.40
[Cu(Anth)(Leu)] · 2H ₂ O	blue	42.4 (42.6)	6.1 (6.0)	—	1.55
[Co(Anth)(Clac)]	beige	37.1 (37.4)	2.9 (2.7)	12.1 (12.2)	3.88
[Ni(Anth)(Clac)]	pale green	37.5 (37.4)	3.1 (2.7)	12.3 (12.2)	3.42
[Cu(Anth)(Clac)]	green	36.6 (36.8)	2.9 (2.7)	12.1 (12.0)	1.78

^a Theoretical values in parentheses
Abbreviations: Anth = anthranilic acid; Leu = leucine; Clac = monochloroacetic acid.

The IR spectra of complexes [Co(Anth)(Leu)] · 4H₂O and [Cu(Anth)(Leu)] · 2H₂O are characterized by bands due to the presence of water. Their $\nu(\text{OH})_{\text{water}}$ band occurs in the range 3480—3500 cm⁻¹; this band is attributed exclusively to lattice water.¹⁶ In the spectra of complexes [Co(Anth)(Leu)] · 4H₂O, [Ni(Anth)(Leu)], and [Cu(Anth)(Leu)] · 2H₂O, the two bands appearing in the region 3110—3310 cm⁻¹ are ascribed to νNH_2 of both anthranilate and leucinate ligands.^{17,18} It is assumed that νNH_2 of anthranilate and that of leucinate fall together in the same region since complexes [Co(Anth)(Clac)], [Ni(Anth)(Clac)], and [Cu(Anth)(Clac)] exhibit two bands in about the same range (3100—3310 cm⁻¹), assignable to νNH_2 of the anthranilate ligand. For the first three mixed ligand complexes of anthranilate and leucinate the asymmetric stretching frequency of COO⁻ in the anthranilate seems to appear in the range 1590—1620 cm⁻¹ and the symmetric mode comes at 1450—1460 cm⁻¹. However, the asymmetric and symmetric modes of COO⁻ in the leucinate ligand could be correlated with the bands at 1540—1560 and 1390—1410 cm⁻¹, respectively.¹⁹

Complexes [Co(Anth)(Clac)], [Ni(Anth)(Clac)], and [Cu(Anth)(Clac)] display a band in the range 1580—1590 cm⁻¹; another band is seen in the region 1450—1460 cm⁻¹. They are assigned to the asymmetric and symmetric stretching vibrations of COO⁻ in the anthranilate ligand, respectively. For the monochloroacetate group in the three complexes the asymmetric and symmetric

frequencies occur in the regions 1530—1540 and 1370 cm^{-1} , respectively. It was found that the difference between the two frequencies, Δ , amounts to 160 or 170 cm^{-1} . It is smaller than the value reported²⁰ for bridging monochloroacetate group, thus indicating that the acetate group acts in these complexes in a bidentate fashion. The most important IR bands of the complexes are given in Table II.

TABLE II
*Pertinent IR Data of the Complexes (cm^{-1})**

Co(Anth)(Neu)·4H ₂ O	3500bh, 3310w, 3140w, 2960m, 1590s, 1540m, 1460m, 1410s, 1050m, 780w, 760m, 720m.
Ni(Anth)(Ueu)	3300m, 3110m, 1610w, 1590s, 1530vs, 1450m, 1410vs, 1320m, 1240m, 1060m, 750vs, 715m, 660m.
Cu(Anth)(Leu)·2H ₂ O	3480br, 3300w, 3240m, 2940m, 1620vs, 1560m, 1450m, 1390m, 1370m, 1130w, 780m, 750m, 710m, 660m.
Co(Anth)(Clac)	3310w, 2140w, 1610w, 1590m, 1530m, 1460vs, 1370vs, 1150w, 1030m, 870m, 750m, 720m, 630m.
Ni(Anth)(Clac)	3280w, 3100w, 1600w, 1580m, 1530m, 1450vs, 1370vs, 1150w, 1050w, 950w, 860m, 740m, 710m, 630m.
Cu(Anth)(Clac)	3240w, 2100w, 1590m, 1540m, 1460vs, 1370vs, 1150m, 950w, 870m, 810m, 750m, 720m.

* w = weak, m = medium, s = sharp, vs = very sharp, br = broad

The electronic spectra (Table III) of the complexes measured in DMSO generally exhibit broad and weak asymmetric d-d bands. They are typical

TABLE III
Electronic Spectra of the Complexes (kK)

Compound	ν_{max} (kK)	Assignment
[Co(Anth)(Leu)]·4H ₂ O	29.2	charge transfer
[Ni(Anth)(Leu)]	23.2	${}^3T_{1g}(\text{P}) \leftarrow {}^3A_{2g}$
	29.4	charge transfer
	37.0	intraligand transition
[Cu(Anth)(Leu)]·2H ₂ O	18.8	d-d
	10.3	charge transfer
[Co(Anth)(Clac)]	14.9	${}^4A_{2g} \leftarrow {}^4T_{1g}(\nu_2)$
	16.6	${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}(\nu_3)$
	29.8	charge transfer
[Ni(Anth)(Clac)]	29.4	charge transfer
[Cu(Anth)(Clac)]	17.8	d-d
	27.9	charge transfer

of distorted octahedral complexes due to the presence of chelating agents which are dissimilar in nature. Keppert²¹ has predicted that normal geometries of the compounds experience distortion as the »bite« of the bidentate ligands changes. Two prominent absorption bands are shown in the spectrum of [Co(Anth)(Clac)] at 14.9 and 16.6 kK, assignable to ${}^4A_{2g} \leftarrow {}^4T_{1g}(\nu_2)$ and ${}^4T_{1g}(\text{P}) \leftarrow$

$\leftarrow {}^4T_{1g}(\nu_3)$ ligand field transitions of Co(II) octahedral structure, respectively. The band at 23.2 kK in the spectrum of [Ni(Anth)(Leu)] represents a ligand field transition of the ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$ type characteristic of octahedral Ni(II) complexes.²² The two copper(II) complexes *vz.* [Cu(Anth)Leu] · 2H₂O and [Cu(Anth)(Clac)] display a broad band at 18.8 and 17.8 kK, respectively. The position and shape of this band suggest the six coordinate geometry around the copper ion. This band may be assigned to all the three transitions ${}^2B_{2g} \leftarrow {}^2B_{1g}$, ${}^2A_{1g} \leftarrow {}^2B_{1g}$, and ${}^2E_g \leftarrow {}^2B_{1g}$, which are usually found for tetragonal copper(II) complexes.²² Bands observed in the range 27.0–30.3 kK for all the complexes are ascribed to charge transfer transitions.

The magnetic moment values of the complexes at room temperature are consistent with an octahedral coordination geometry. The magnetic susceptibilities of four compounds, namely [Cu(Anth)(Leu)] · 2H₂O, [Ni(Anth)(Clac)], [Cu(Anth)Clac], and [Co(Anth)(Clac)], have been determined over the temperature range 80–300 kK. Compound [Cu(Anth)(Leu)] · 2H₂O shows a Curie-Weiss dependence in the range 80–200 K, while the latter three complexes exhibit this dependence in the range 80–300 K; their Θ values are included in Table IV. The magnetic moments show only a very small temperature

TABLE IV
Variable Temperature Magnetic Susceptibility Data on the Complexes

Temp. (K)	$\chi \times 10^{-6}$	χ^{-1}	μ_{eff} (B. M.)
[Cu(Anth)(Leu)] · 2H ₂ O			
80	4067.27	245.86	1.62
100	3134.42	319.03	1.59
120	2546.72	392.66	1.57
140	2210.80	452.32	1.58
160	1959.01	510.46	1.59
180	1676.25	596.56	1.56
200	1470.19	680.18	1.54
220	1389.12	719.87	1.57
240	1322.48	756.15	1.60
260	1190.43	840.03	1.58
280	1077.59	927.99	1.56
300	992.89	1007.15	1.55
$\Theta = 18^\circ\text{C}$			
Co(Anth)(Clac)			
80	22378.992	44.684	3.80
100	18186.991	54.984	3.83
120	15076.787	66.327	3.82
140	13058.633	76.577	3.84
160	11366.869	87.974	3.83
180	9998.636	100.013	3.81
200	9141.043	109.396	3.84
220	8353.377	119.712	3.85
240	7697.092	129.919	3.86
260	7141.869	140.019	3.87
280	6631.735	150.790	3.87
300	6221.649	160.729	3.88
$\Theta = 72^\circ\text{C}$			

Table IV continued.

Temp. (K)	$\chi \times 10^{-6}$	χ^{-1}	μ_{eff} (B. M.)
Ni(Anth)(Clac)			
80	17288.856	57.840	3.34
100	13748.388	72.735	3.33
120	11525.904	86.761	3.34
140	9879.346	101.221	3.34
160	8696.268	114.991	3.35
180	7730.016	129.365	3.35
200	7040.331	142.038	3.37
220	6438.340	155.319	3.38
240	5971.860	167.451	3.40
260	5544.960	180.343	3.41
280	5148.890	194.216	3.41
300	4833.860	206.873	3.42
$\theta = 48^\circ\text{C}$			
Cu(Anth)(Clac)			
80	4584.903	218.107	1.72
100	3753.719	266.402	1.74
120	3164.158	316.039	1.75
140	2681.228	372.963	1.74
160	2346.074	426.243	1.74
180	2061.498	485.084	1.73
200	1876.859	532.804	1.74
220	1725.904	579.406	1.75
240	1600.211	624.917	1.76
260	1493.951	669.365	1.77
280	1387.240	720.855	1.77
300	1309.429	763.691	1.78
$\theta = 66^\circ\text{C}$			

dependence, probably originating from zero-field effects. At room temperature the complex $[\text{Cu}(\text{Anth})(\text{Leu})] \cdot 2\text{H}_2\text{O}$ has a magnetic moment value (μ_{eff}) of 1.55 B. M., which is evidently rather lower than expected for spin-only value of Cu(II) (1.73 B. M.).²³ This may indicate some spin-spin interaction in the solid state between the copper atoms in the complex. The two cobalt complexes $[\text{Co}(\text{Anth})(\text{Leu})] \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{Anth})(\text{Clac})$ exhibit at room temperature magnetic values of 3.83 and 3.88 B. M., respectively. The magnetic moment of Co(II) ion, which has ${}^4\text{T}_{1g}$ ground term in the octahedral field, is expected to be associated with a large orbital contribution and hence show a value as large as 5.20 B. M. The lower magnetic moments can be explained on the basis of low symmetry components which tend to quench the orbital contribution and the value approaches the spin-only value.²³

The thermal behaviour of the complexes was studied over the temperature range 50–600°C. The mixed ligand complexes of leucinate exhibit a great thermal stability; they begin to decompose at 370–400°C. The mixed ligand complexes of monochloroacetate possess, however, a lower thermal stability than the leucinate complexes as they decompose at 250–280°C. The TGA thermograms of the complexes consist of a number of decomposition steps, which have the corresponding endothermic or exothermic peaks in the

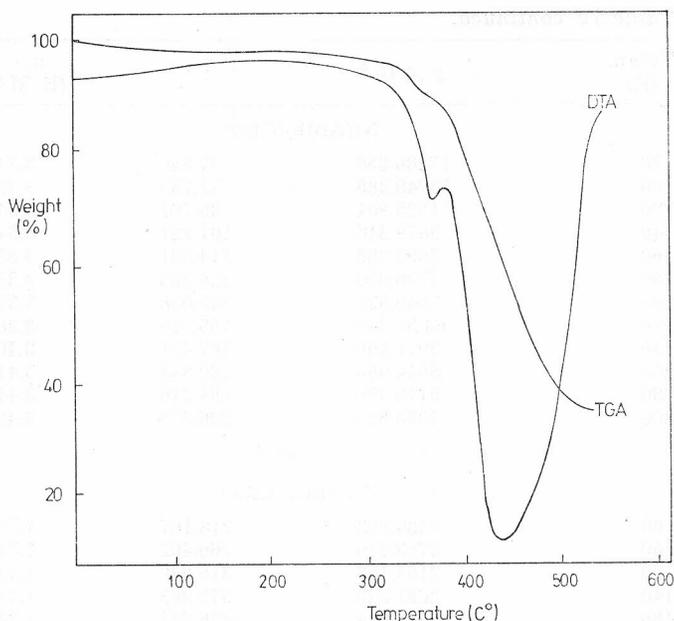


Figure 1. TGA and DTA thermograms of $[\text{Ni}(\text{Anth})(\text{Leu})]$.

DTA curves. Figure 1 illustrates the TGA and DTA thermograms of $[\text{Ni}(\text{Anth})(\text{Leu})]$ with two endothermic peaks corresponding to two decomposition steps.

In view of the above discussion we suggested the structure of the complexes as depicted in Figure 2; a polymerization as an alternate molecular association was proposed, through which the metal ions attain their six-coordinate geometry.

EXPERIMENTAL

Anthranilic acid, leucine, monochloroacetic acid, cobalt(II) chloride, nickel(II) chloride, and copper(II) chloride were of reagent grade.

Preparation of the Complexes

The preparation of the complexes followed essentially the following procedure: A solution of anthranilic acid (8 mmol) in 20 ml hot water was added to a 20 ml hot solution of the respective metal chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (4 mmol) in water. The pH was adjusted at 7–8 using ammonia solution where a precipitation of the binary complexes occurs; the mixture was refluxed for about one hour. A solution (4 mmole) of leucine or monochloroacetic acid in 30 ml water was then added dropwise at continuous stirring to the mixture; an immediate change of colour was observed. The reaction mixture was refluxed for one hour and the product was filtered, washed with warm water and dried in vacuo over P_4O_{10} .

Physical Measurements

The infrared spectra were measured as KBr pellets on a Perkin Elmer 599B spectrophotometer. Electronic spectra in dimethylsulphoxide solutions were recorded on a Shimadzu 200S spectrophotometer. Magnetic measurements were obtained

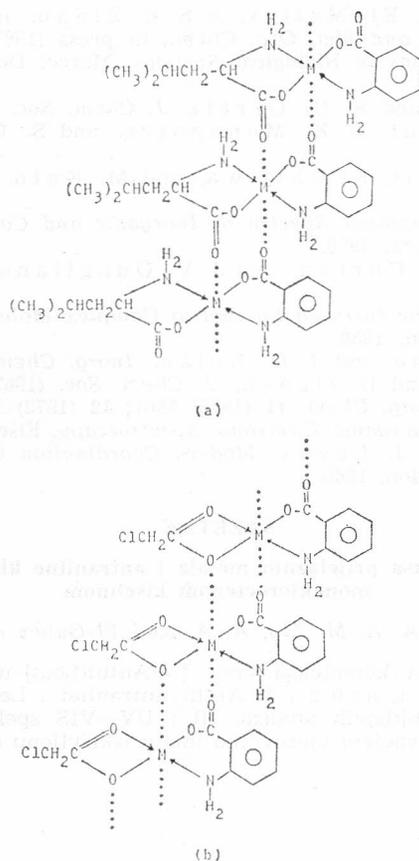


Figure 2 (a and b). Suggested structures of the complexes.

by the Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. Diamagnetic corrections were made using Pascal's constants. Thermal measurements were carried out on a Heraeus DTA 500 thermal analyzer, with a furnace heating rate of 10°C per minute.

REFERENCES

1. S. S. Sandhu, B. S. Manhas, M. R. Mittal, and S. S. Parmar, *Indian J. Chem.* **7** (1969) 286.
2. Y. H. Deshpande and V. R. Rao, *Indian J. Chem.* **7** (1969) 1051.
3. T. V. Shestakova, Z. N. Prozorovskaya, and L. N. Komissarova, *Zh. Neorg. Khim.* **19** (1974) 2671.
4. C. S. Pande and G. N. Misra, *J. Indian Chem. Soc.* **51** (1974) 835.
5. B. Kim, C. Miyake, and S. Imoto, *J. Inorg. Nucl. Chem.* **36** (1974) 2015.
6. E. A. Bayazitova, V. V. Zelentsov, and V. I. Spitsyn, *Zh. Strukt. Khim.* **8** (1967) 496.
7. R. L. Dutta and D. De, *J. Indian Chem. Soc.* **46** (1969) 62.
8. S. N. Limaye and M. C. Saxena, *Can. J. Chem.* **64** (1986) 865.
9. A. A. M. Aly, A. A. Mohamed, M. A. Mousa, and M. El-Shabasy, *Chem. Scripta* **24** (1984) 196.
10. A. A. Mohamed, A. A. M. Aly, and M. El-Shabasy, *Croat. Chem. Acta* **59** (1986) 509.

11. A. A. M. Aly, M. S. El-Meligy, A. S. A. Zidan, and M. El-Shabasy, *Synth. React. Inorg. and Met. Org. Chem.*, in press (1987).
12. H. Sigel, *Metal Ions in Biological Systems*, Marcel Dekker, New York, 1973, Vol. 2, p. 101.
13. C. A. Agamber and K. G. Orrell, *J. Chem. Soc. (A)* (1969) 897.
14. C. D. Rao, B. Paul, B. K. Mohapatra, and S. Gurv, *J. Inorg. Nucl. Chem.* **40** (1978) 134.
15. Y. Muto, T. Tokii, K. Chijiwa, and M. Kato, *Bull. Chem. Soc. Jpn.* **57** (1984) 1011.
16. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, 1970.
17. G. F. Svatos, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.* **79** (1957) 3313.
18. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed, Methuen and Co. Ltd., London, 1958.
19. S. E. Livingstone and J. D. Nolan, *Inorg. Chem.* **7** (1968) 1447.
20. A. B. P. Lever and D. Ogden, *J. Chem. Soc.* (1967) 2041.
21. D. L. Kepert, *Inorg. Chem.* **11** (1972) 1561; **12** (1973) 1944.
22. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968.
23. B. N. Figgis and J. Lewis, *Modern Coordination Chemistry*, Interscience Publishers Ltd., London, 1960.

SAŽETAK

Reaktivnost kompleksa prijelaznih metala i antranilne kiseline s leucinom i monokloroocetenom kiselinom

A. M. El-Roudi, A. A. M. Aly, A. A. Abd El-Gaber i M. El-Shabasy

Pripremljeno je šest kompleksa vrste $[M(\text{Anth})(\text{Leu})] \cdot n\text{H}_2\text{O}$ i $[M(\text{Anth})(\text{Clac})]$ u kojima $M = \text{Co}$, Ni i Cu ; $n = 0$ 2 i 4; $\text{Anth} = \text{antranilat}$ i $\text{Leu} = \text{leucinat}$. Kompleksi su opisani na temelju njihovih analiza, IR i UV—VIS spektara, te magnetskih i termičkih mjerenja. Svi spojevi vjerovatno imaju iskrivljenu oktaedarsku, polimernu strukturu.