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# STUDIES ON COMPLEXES OF METAL(II) CARBOXYLATES WITH DONOR MOLECULES-V COMPLEXES OF COBALT(II), NICKEL(II) AND COPPER(II) ARYL CARBOXYLATES WITH PICOLINE N-OXIDES

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Interaction of various metal(II) aryl carboxylates with picoline N-oxides afforded 1 : 1 adducts $M(O_2CC_6H_4Z)_2L$ where M = Co(II), Ni(II), Cu(II) and Z = H or $CH_3$-o & p, $CH_3O$-p, Cl-o-, m- & p. Conductance and molecular weight studies indicate that the complexes are neutral dimeric species. Magnetic and spectral studies show that they are magnetically condensed, carboxylate bridged species in which magnetic interaction increases with increasing basicity of the aryl carboxylate anion.

**Keywords : Metal(II) Aryl Carboxylates; 2- & 3-Picoline N-Oxide Complexes**

## INTRODUCTION

IN contrast to their parent heterocyclic amines, which yield complexes of 1 : 1, 1 : 2 and 1 : 4 stoiehiometry with metal(II) carboxylates (Amasa *et al.*, 1969; and Lever & Ogden, 1967), pyridine N-Oxides invariably afford 1 : 1 complexes with these systems (Kumar *et al.*, 1979, 1980). This peculiar behaviour of these ligands is believed to stem from their relatively low σ-donorability and high π-acceptorability (Hibdon & Nelson, 1973). In the present investigation, complexes of 2- & 3-Picoline N-Oxides were prepared with Co(II), Ni(II) and Cu(II) aryl carboxylates to study their structure utilizing magnetic and spectral techniques.

## MATERIALS AND METHODS

Pyridine N-Oxides were obtained commercially (Fluka AG). Cobalt(II) aryl carboxylates were generated in solution while nickel(II) and copper(II) aryl carboxylates were isolated as solid samples using literature methods (Drew *et al.*, 1973; and Lewis *et al.*, 1965).

Metal contents of the complexes were determined by the authors using standard gravimetric procedures (Vogel, 1962). C and H were determined microanalytically. Conductivity measurements were carried out with a Philips GM 4144/90 conductivity bridge in MeOH and $PhNO_2$. Molecular weights, where feasible, were determined cryoscopically in $PhNO_2$. Magnetic moments were determined at room temperature by Gouy's method. Electronic Spectra were recorded on a Beckman DK-2A spectrophotometer using 1 cm quartz cells. Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer.

*Preparation of Complexes* :

The complexes of metal(II) aryl carboxylates were prepared by mixing the respective carboxylate with the appropriate ligand in 1 : 1 molar ratio in an organic medium with or without refluxing. In preparing cobalt(II) complexes the ligands were added to the fresh cobalt(II) aryl carboxylate generated in solution by refluxing a solution of the appropriate carboxylic acid in methanol with basic cobalt carbonate for 12–16 hours and filtering off the unreacted cobalt carbonate. Nickel and copper(II) complexes were obtained by refluxing the ligands with a suspension of a solution of the appropriate carboxylate in acetone. The filtered solution of the reaction mixture on concentration and allowing to stand overnight invariably deposited a solid crystalline product. It was separated, recrystallized or washed several times with the solvent used in their preparation and dried under vacuum or at atmospheric pressure at ambient temperatures over $P_2O_5$.

Molar conductance, magnetic moments and electronic spectra of the complexes prepared are given in Table I.

## Results and Discussion

The complexes were shown by analysis to correspond to 1 : 1 stoichiometry of general formula $M(O_2CC_6H_4R)_2L$ where M is Co(II), Ni(II), Cu(II); L is 2– or 3-Picoline N-Oxide and R is H; o- & p-$CH_3$; o- & m-Cl; p-$OCH_3$.

Cobalt complexes are red or pink in colour while nickel and copper form either green or blue complexes. Excepting nickel complexes all others are soluble in polar solvents. Their molar conductance values (Table I) show that the complexes are covalent in nature. Molecular weights of bis(p-methoxy benzoate) (2-PicNO)cobalt(II) and bis(p-methoxy benzoate)-(2-Pic NO) copper(II) in $PhNO_2$ were found to be 945 and 948 respectively, which are more than twice the values of their respective monomeric formula weights, indicating that these complexes are dinuclear of carboxylate bridged structure.

The magnetic moments of Co(II), Ni(II) and Cu(II) complexes fall in the ranges of 4.00–4.26, 2.50–2.67 and 1.38–1.52 B. M. respectively (Table I). These values are lower than the values of 4.88–5.15, 3.15–3.35, 1.90–2.15 B.M. generally found in their magnetically normal octahedral complexes (Lever & Ogden, 1967) suggesting that all of these complexes are dinuclear of carboxylate bridged structure similar to various other 1 : 1 dimeric complexes of metal(II) carboxylates (Jotham *et al.*, 1972; and Drew *et al.*, 1973). However, magnetic moments of the complexes show a tendency to increase with decreasing basicity of the carboxylate anion.

In their electronic spectra cobalt and nickel complexes show three bands while copper complexes exhibit two bands only. The shapes and positions of the three bands observed in cobalt and nickel(II) complexes (Table I) are such that the complexes can be safely considered to possess a distorted octahedral stereochemistry (Lever, 1968). The two bands (I & II) occurring around 14,000 and 16,000 $cm^{-1}$ in the electronic spectra of copper(II) complexes point that these complexes are also dimeric carboxylate bridged species and these two bands originate from $d_{xz,yz} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions respectively (Hibdon & Nelson, 1973; and Lever, 1968).

TABLE I

*Molar Conductivity, magnetic and electronic spectral data of the Picoline N-oxide complexes of metal (II) aryl carboxylates*

| Sr. No. | Complex* | Conductivity mho cm² mole⁻¹ | $\mu_{eff}$ B.M. (290K) | Electronic Spectra ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|
| | | | | *Complexes of Cobalt(II) Aryl Carboxylates* | | |
| | | | | $4T_{2g}(F) \leftarrow 4T_{1g}(F)$ | $4A_{2g}(F) \leftarrow 4T_{1g}(F)$ | $4E_g(P) \leftarrow 4T_{1g}(F)$; $4A_{2g} \leftarrow 4T_{1g}(F)$ |
| 1. | $[Co(O_2CC_6H_5)_2 2\text{-PicNO}]_2$ | 20.65 | 4.09 | 8585; 8810 | 16,130 | 19,620; 21,275(Sh) |
| 2. | $[Co(O_2CC_6H_5)_2 3\text{-PicNO}]_2$ | 19.05 | 4.12 | 8620; 8850 | 17,240(Sh) | 19,610; 21,055(Sh) |
| 3. | $[Co(O_2CC_6H_4CH_3\text{-p})_2 2\text{-PicNO}]_2$ | 18.37 | 4.05 | 8630; 8870 | 17,250 | 19,630; 21,060(Sh) |
| 4. | $[Co(O_2CC_6H_4CH_3\text{-p})_2 3\text{-PicNO}]_2$ | 17.20 | 4.06 | 8625; 8860 | — | 19,530; 21,285(Sh) |
| 5 | $[Co(O_2CC_6H_4OCH_3\text{-p})_2 2\text{-PicNO}]_2$ | 20.07 | — | 8610; 8775 | 17,095(Sh) | 19,600; 21,270(Sh) |
| 6. | $[Co(O_2CC_6H_4OCH_3\text{-p})_2 3\text{-PicNO}]_2$ | 21.81 | 4.00 | 8615; 8890 | 17,100(Sh) | 19,605; 20,835(Sh) |
| 7. | $[Co(O_2CC_6H_4Cl\text{-o})_2 2\text{-PicNO}]_2$ | 20.17 | 4.22 | 8550; 8820 | 17,300 | 19,610; 21,065(Sh) |
| 8. | $[Co(O_2CC_6H_4Cl\text{-o})_2 3\text{-PicNO}]_2$ | 25.11 | 4.25 | 8585; 8830 | 17,260(Sh) | 19,240; 20,620(Sh) |
| | | | | *Nickel(II) Aryl Carboxylate Complexes* | | |
| | | | | $3T_{2g}(F) \leftarrow 3A_{2g}$ | $3T_{1g}(F) \leftarrow 3A_{2g}$ | $3T_{2g}(P) \leftarrow 3A_{2g}$ |
| 9. | $[Ni(O_2CC_6A_6)_2 2\text{-PicNO}]_2$ | 16.71 | 2.58 | 8810 | 13,425; 14,750 | 24,640 |
| 10. | $[Ni(O_2CC_6H_5)_2 3\text{-PicNO}]_2$ | 18.26 | 2.61 | 8770 | 13,520; 14,575 | 24,740 |
| 11. | $[Ni(O_2CC_6H_4CH_3\text{-p})_2 2\text{-PicNO}]_2$ | 15.48 | 2.48 | 8995 | 13,160; 14,705 | 24,155 |
| 12. | $[Ni(O_2CC_6H_4CH_3\text{-p})_2 3\text{-PicNO}]_2$ | 16.36 | 2 50 | 8875 | 13,245; 14,665 | 24,510 |
| | | | | *Copper(II) Aryl Carboxylate Complexes* | *Band I* | *Band II* |
| 13. | $[Cu(O_2CC_6H_4CH_3\text{-o})_2 2\text{-PicNO}]_2$ | 35.21 | 1.39 | | 14,425[a]<br>13,990[b] | —<br>25,850(Sh) |
| 14. | $[Cu(O_2CC_6H_4CH_3\text{-p})_2 2\text{-PicNO}]_2$ | 25.56 | 1.40 | | 13,905[a]<br>13,400[b] | —<br>25,420(Sh) |
| 15. | $[Cu(O_2CC_6H_4CH_3\text{p-})_2 3\text{-PicNO}]_2$ | 33.28 | 1.42 | | 14,045[a]<br>13,890[b] | —<br>27,030(Sh) |
| 16. | $[Cu(O_2CC_6H_4OCH_3\text{-p})_2 2\text{-PicNO}]_2$ | 38.73 | 1.37 | | 13,890[a]<br>13,795[b] | —<br>25,650(Sh) |
| 17. | $[Cu(O_2CC_6H_4OCH_3\text{-p})_2 3\text{-PicNO}]_2$ | 26.64 | 1.37 | | 14,165[a]<br>14,490[b] | —<br>26,320(Sh) |
| 18. | $[Cu(O_2CC_6H_4Cl\text{-o})_2 2\text{-PicNO}]_2$ | 38.63 | 1.50 | | 13,700[a]<br>13,795[b] | —<br>25,640(Sh) |
| 19 | $[Cu(O_2CC_6H_4Cl\text{-m})_2 2\text{-PicNO}]_2$ | 31.03 | 1.52 | | 13,910[a]<br>14,490[b] | —<br>26,350(Sh) |

*C, H, and Metal contents of the complexes were found within permissible limits of their theoretical values and mean deviation from the average for C, H, and Metal contents was 0.39, 0.36 and 0.19 respectively.

Sh, Shoulder; a, methanol; b, benzene.

The negative shifts of 15–50 $cm^{-1}$ observed in N—O stretching frequency of the Picoline N-Oxides in the complexes indicate that they coordinate through their N—O oxygen (Karayannis *et al.*, 1973). The difference of 210 $cm^{-1}$ in their asymmetric and symmetric COO stretching frequencies, which fall around 1605 and 1395 $cm^{-1}$, indicates that the carboxylate moiety in these systems behaves as a bidentate bridging group implying that the complexes under study are binuclear carboxylate bridged species like so many other 1 : 1 adducts of metal(II) aryl carboxylates reported earlier (Herring *et al.*, 1971; and Bose & Patel, 1970).

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