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SYNTHESIS, MAGNETIC AND SPECTROSCOPIC CHARACTERIZATION OF METAL(II) ARYLCARBOXYLATE ADDUCTS WITH SATURATED HETEROCYCLIC BASES

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Abstract—Several new complexes of $M(RCOO)_2$ (where $R = C_6H_5$, 2-, 3- or 4-$O_2NC_6H_4$ and M = Co, Ni or Cu) with saturated diheterocyclic bases (L—L) of the type $M(RCOO)_2(L—L)_n$ (where $n = 2$, 1 or 0.5 and L—L = piperazine, 1-methylpiperazine, 2-methylpiperazine, 1-phenylpiperazine, 2,6-dimethylpiperazine, 2,5-dimethylpiperazine, 1,4-dimethylpiperazine and 4-methylmorpholine) and with saturated monoheterocyclic bases (L) of the type $M(RCOO)_2L_n$ (where $n = 2$ or 1 and L = 2-methylpiperidine, 3-methylpiperidine and 4-methylpiperidine) have been synthesized and characterized by elemental analyses, IR and electronic reflectance spectral and magnetic susceptibility measurement studies. In addition, most of the copper(II) complexes are also characterized by EPR spectral measurements. All complexes of cobalt(II) and nickel(II) are found to be magnetically dilute except $Co(2\text{-}O_2NC_6H_4COO)_2$(4Me-morl) (where 4Me-morl = 4-methylmorpholine) which is antiferromagnetic. Copper(II) forms both magnetically dilute and antiferromagnetic complexes with these bases. Probable structures have been assigned to all these complexes. The spin-exchange parameter, $-2J$, for antiferromagnetic complexes has been evaluated from both magnetic susceptibility and EPR measurements at different temperatures. No correlation between the value of $-2J$ and pK_a of the acid or terminal ligand could be established.

There has been considerable interest in the chemistry of metal(II) carboxylates and their complexation properties with nitrogen and oxygen donor ligands.[1–7] Depending upon the structure, the complexes show different magnetic behaviour. Many factors such as stoichiometry,[3,5] nature of carboxylic acid,[3,6,7] steric and electronic characteristics of the additional ligand[8–13] and conditions of the reaction[14] determine the structural priorities of the complex.

A literature survey reveals that although some workers have examined the role of "steric hindrance" or electronic nature of the substituent group on the pyridine type ligands[3,5–9] in their complexation behaviour with cobalt(II), nickel(II) and copper(II) carboxylates, no such systematic effort has yet been made for the saturated diheterocyclic bases (L—L) and monoheterocyclic bases (L). So the present work on the synthesis and magnetic and spectral properties for complexes of $M(RCOO)_2$ (where M = Co, Ni and Cu and $R = C_6H_5$, 2-, 3- or 4-$O_2NC_6H_4$) with ligands of different steric and electronic characteristics such as piperazine (pipz), 1-methylpiperazine (1Me-pipz), 2-methylpiperazine (2Me-pipz), 1-phenylpiperazine (1Ph-pipz), 1,4-

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dimethylpiperazine (1,4Me_2-pipz), 2,5-dimethylpiperazine (2,5Me_2-pipz), 2,6-dimethylpiperazine (2,6Me_2-pipz) and 1-methylmorpholine (1Me-morl), L—L; and 2-methylpiperidine (2Me-pipd), 3-methylpiperidine (3Me-pipd) and 4-methylpiperidine (4Me-pipd), L, has been undertaken. An additional incentive to undertake these studies was to see if the boat form of the diheterocyclic base could be stabilized in the complexed state.

EXPERIMENTAL

Starting materials

Liquid heterocyclic bases such as 1Me-pipz, 1Ph-pipz, 1,4Me_2-pipz (all from Fluka), 4Me-morl and 2-, 3- and 4Me-pipd's (all from K and K Laboratories) were dried by refluxing and distilling over sodium hydroxide pellets before use. Solid ligands viz. pipz, 2Me-pipz, 2,6Me_2-pipz and 2,5Me_2-pipz (K and K Laboratories) were kept over potassium hydroxide pellets in a vacuum desiccator for 3 days to dry. The purity of 2-, 3- and 4-nitrobenzoic acids (BDH, LR) was checked from their sharp melting points after recrystallization from ethanol. Other materials such as metal(II) chlorides (BDH) or sodium benzoate (BDH, AR) were used as such without any purification. Acetone, *n*-hexane, solvent ether and petroleum ether (40–60°C), all from BDH, were purified by the usual methods.

Preparation of metal(II) *nitrobenzoates*

A solution of nitrobenzoic acid (10.0 g, 60 mmol) in a minimum quantity of acetone was neutralized with aqueous sodium hydroxide solution. A small quantity (20 mg) of the nitrobenzoic acid was added to make the solution just acidic and the solution was then filtered. The stirring, aqueous solution of sodium nitrobenzoate thus formed was added to a filtered aqueous solution of metal(II) chloride ($\simeq$ 7 g, 30 mmol). All three copper(II) nitrobenzoates, cobalt(II) 3- and 4-nitrobenzoates and nickel(II) 4-nitrobenzoate separated out after the contents had been stirred for 0.5 h. Other metal(II) nitrobenzoates were obtained upon concentrating the reaction mixture and cooling it in a refrigerator. The separated product was filtered, washed with cold distilled water and dried in air. The air-dried product was then subjected to vacuum at 140°C for 4 h.

Copper(II) benzoate was similarly prepared by reacting sodium benzoate with copper(II) sulphate in water, which separated upon mixing the contents.

Preparation of complexes

A solution of the stoichiometric amount in general, and in the case of 1,4Me_2-pipz and 4Me-morl a 50% excess, of the saturated heterocyclic base dissolved in acetone (15 cm^3) was added dropwise to a continuously stirred solution/suspension of metal(II) carboxylate (1 g) in acetone (*ca* 50 cm^3). Most of the adducts of the diheterocyclic bases separated on stirring for 0.5 h, and these were completely precipitated by the addition of *n*-hexane or ether. Other complexes were separated on concentrating the reaction mixture to about a quarter of its original volume, cooling in the refrigerator for 4 h and adding solvent ether or *n*-hexane. The separated product was filtered through a G_4 filtration unit, washed with solvent ether and *n*-hexane, and dried under vacuum.

Elemental analyses and physical measurements

The metal content in the complexes was determined volumetrically by EDTA titration using Xylenol Orange as indicator. Carbon and hydrogen analyses were performed on an automatic Coleman-33 analyser, while nitrogen was estimated by Kjeldahl's method in the departmental microanalytical laboratory.

Room-temperature magnetic susceptibility of all the complexes was measured on a Gouy balance using $Hg[Co(NCS)_4]$ as calibrant. The magnetic susceptibility of some representative cobalt(II) complexes and antiferromagnetic copper(II) complexes at different temperatures was measured on a Curie Magnetic susceptibility with the NEC PC-980 Data Treatment System or on a Vibrating Sample Magnetometer (VMS) PAR-155 with a variable-temperature cryostat. The measured susceptibility was corrected for the diamagnetic susceptibility of the ligands. The correction for temperature independent paramagnetism was taken as -60×10^{-6} c.g.s. units per gram atom of copper(II) ions.

IR spectra of the acids, their anhydrous metal(II) and sodium salts and the complexes were recorded both as Nujol and hexachlorobutadiene mulls on an IR-20 spectrophotometer with sodium chloride plates as windows in the 4000–600 cm^{-1} region, while far-IR spectra in the range 600–250 cm^{-1} were measured as Nujol mulls in polythene film. Electronic reflectance spectra of the complexes were recorded on Unicam SP-700 UV–vis–near IR spectrophotometer with a SP-735 diffuse reflectance attachment. The EPR measurements of powdered samples at liquid nitrogen temperature (77 K) were carried out on a Varian E-4 EPR-spectrometer at X-band frequencies (8.8–9.6 GHz). The X-band EPR measurements of powdered materials of antiferromagnetic complexes at different temperatures were made on a Varian E-12 EPR spectrometer using the E-257 variable-temperature assembly. Diphenylpicrylhydrazyl (DPPH) was used as calibrant.

The pK_as of some of the bases were determined pH-metrically at 37°C using an Elico (model 4-122) digital meter.

RESULTS AND DISCUSSION

Chemical formulae based upon elemental analyses, colour and room-temperature μ_{eff} values are listed in Table 1. Examination of Table 1 shows that these metal(II) carboxylates give rise to complexes of 1:0.5, 1:1 or 1:2 (metal–base) stoichiometry with these saturated heterocyclic bases. The different complexation behaviour of these bases will be discussed later. All complexes of cobalt(II) are red, pink or brown, except Co(3-$O_2NC_6H_4$COO)$_2$(2Me-pipd) which is green, while nickel complexes are green or pale green. Most of the copper(II) complexes are blue or light blue except for the antiferromagnetic complexes (**XCVII–CXI**) which are green.

IR spectral studies

Various structural possibilities for complexes of the stoichiometries M(RCOO)$_2$L$_n$ (where $n = 2$, 1 or 0.5) which depend upon the mode of coordination of the carboxylate group and the diheterocyclic base, have been discussed elsewhere.[15] IR studies are quite useful in determining the mode of coordination of these ligands.[5,16] On critically examining the positions and direction of the shifts of the ν_{as}(OCO) and ν_s(OCO) of the carboxylate group in the complexes, as compared to their positions in the sodium salts of the respective acids, the bridging bidentate mode for complexes **XIX**, **XLV**, **XLVII**, **XLIX** and **LVII** and, **XCVII–CXI** and the chelating bidentate mode of coordination of the carboxylate group for all other complexes can be suggested.[16,17] A shift to the lower energy region ($\simeq$ 50 cm^{-1}) of the bands due to ν(N—H) vibrations in the complexes relative to those in the free bases ($\simeq$ 3300 cm^{-1}) indicates the coordination of the bases through the nitrogen atom(s) of their N—H bond(s).[18,20] However, in the IR spectrum of 1Me-pipz complexes of the type M(RCOO)$_2$(1Me-pipz)$_2\cdot$2H$_2$O, this band is much too broad (due to it becoming mixed into ν(O—H) and enhanced effect of hydrogen bonding) to indicate any shift. An examination of the band around 2750 cm^{-1} due to ν(C—H) of N—CH$_3$ in the complexes of 1Me-pipz, 1,4Me$_2$-pipz and 1Me-morl shows that this band is observed at almost the same position as in the free bases for complexes of the type M(RCOO)$_2$(1Me-pipz)$_2$ or Cu(RCOO)$_2$(1Me-pipz) which indicates that the nitrogen atom of the N—CH$_3$ group remains uncoordinated, while this frequency disappears or undergoes large positive shifts for other complexes of these bases, showing the binding of this nitrogen atom to the metal.[20,21]

Additional bands in the complexes, compared with the IR spectra of uncomplexed metal(II) carboxylates and free bases in the region 370–440 cm^{-1} and 320–360 cm^{-1}, have tentatively been assigned to ν(M—O) and ν(M—N) modes, respectively.[18,19,22–24] In the region of absorption of diheterocyclic bases, the IR spectra of the complexes under study closely resemble those of the free bases, and no additional bands characteristic of the boat form are observed. This indicated that the ligands are coordinated in the chair form.[25,26]

Electronic reflectance spectral studies

All cobalt(II) complexes in the present study, other than Co(3-$O_2NC_6H_4$COO)$_2$(2Me-pipd) or **XXX** and Co(2-$O_2NC_6H_4$COO)$_2$(4Me-morl) or **XIX**, show two principal absorption bands around 8000 cm^{-1} (ν_1) and 19,000 cm^{-1} (ν_3) which are assigned, respectively, to the $^4T_{2g} \leftarrow {}^4T_{1g}(F)$ and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transitions for the cobalt(II) ion in approximate octahedral environments (Fig. 1).[8,27] A weak band or a shoulder observed around 15,000 cm^{-1} (ν_2) for some of the complexes is assigned to the third spin-allowed but two-electron forbidden $^4A_{2g} \leftarrow {}^4T_{1g}(F)$ transition. The ratio of ν_2/ν_1 for these complexes lies in the range 1.9–2.10, which lends support to the above assignments.[27,28] The broadness or splitting observed for the ν_1 band can be attributed to the distortion of structure from cubic symmetry. The Dq and B values for these complexes (calculated from ν_3/ν_1) lie in the range 870–950 and 750–900 cm^{-1}, respectively.[8,18] Electronic diffuse reflectance spectra of **XIX** and **XXX** are similar to those of square-pyramidal and trigonal-bipyramidal environments around the cobalt(II) ion, respectively.[8]

All nickel(II) complexes under present discussion show bands around 8700 (ν_1) 14,000 (ν_2) and 26,000 (ν_3) cm^{-1} (but some show the last band around 21,000 cm^{-1}, viz. **XL**, **XLVIII**, **L** and **LXI**) in their electronic diffuse reflectance spectra. The number, shape and energies of these bands are the characteristics of *trans*-pseudo octahedral structure (D_{4h} symmetry) containing the NiO$_4$N$_2$ chromophore and are, therefore, assigned to the $^3T_{2g} \leftarrow {}^3A_{2g}(\nu_1)$,

Table 1. Elemental analysis data (%),[a] colour and room-temperature μ_{eff} values of the complexes

Complex	M	C	H	N	Colour	μ_{eff}
$Co(4\text{-}O_2NC_6H_4COO)_2$(pipz) (**I**)	11.9(12.4)	44.8(45.3)	4.1(3.8)	12.0(11.7)	Light brown	4.67
$Co(4\text{-}O_2NC_6H_4COO)_2$(1,4$Me_2$-pipz) (**II**)	11.4(11.7)	47.2(47.5)	4.4(4.4)	11.2(11.0)	Light pink	4.70
$Co(4\text{-}O_2NC_6H_4COO)_2$(1Me-pipz)$_2 \cdot 2H_2O$ (**III**)	9.1(9.4)	46.0(45.9)	5.4(5.7)	13.6(13.4)	Light orange	4.65
$Co(4\text{-}O_2NC_6H_4COO)_2$(2Me-pipz) (**IV**)	11.8(12.0)	46.4(46.4)	4.2(4.1)	11.7(11.4)	Light orange	4.64
$Co(4\text{-}O_2NC_6H_4COO)_2$(1Ph-pipz)$_2$ (**V**)	8.4(8.2)	57.3(57.0)	5.2(5.3)	11.7(11.8)	Brown	4.75
$Co(4\text{-}O_2NC_6H_4COO)_2$(2,6$Me_2$-pipz) (**VI**)	11.5(11.7)	47.8(47.5)	4.7(4.4)	11.3(11.1)	Light violet	4.74
$Co(4\text{-}O_2NC_6H_4COO)_2$(2,5$Me_2$-pipz) (**VII**)	11.4(11.7)	47.3(47.5)	4.6(4.4)	11.4(11.1)	Brown	4.58
$Co(4\text{-}O_2NC_6H_4COO)_2$(4Me-morl) (**VIII**)	11.8(12.0)	46.1(46.3)	4.1(3.9)	8.2(8.5)	Light pink	4.98
$Co(4\text{-}O_2NC_6H_4COO)_2$(2Me-pipd) (**IX**)	11.8(12.0)	48.4(49.0)	4.4(4.3)	8.8(8.6)	Brown	4.61
$Co(4\text{-}O_2NC_6H_4COO)_2$(3Me-pipd)$_2$ (**X**)	9.9(11.0)	53.2(53.0)	5.8(5.8)	9.3(9.5)	Reddish-violet	4.64
$Co(4\text{-}O_2NC_6H_4COO)_2$(4Me-pipd)$_2$ (**XI**)	10.1(10.0)	53.1(53.0)	5.9(5.8)	9.4(9.5)	Violet	4.84
$Co(2\text{-}O_2NC_6H_4COO)_2$(pipz) (**XII**)	12.0(12.4)	44.9(45.3)	3.9(3.7)	11.5(11.7)	Light pink	4.89
$Co(2\text{-}O_2NC_6H_4COO)_2$(1Me-pipz)$_2 \cdot 2H_2O$ (**XIII**)	9.2(9.4)	45.6(45.9)	5.5(5.7)	13.1(13.4)	Pink	4.90
$Co(2\text{-}O_2NC_6H_4COO)_2$(2Me-pipz) (**XIV**)	11.8(12.0)	46.6(46.4)	4.2(4.0)	11.1(11.4)	Violet	4.72
$Co(2\text{-}O_2NC_6H_4COO)_2$(1Ph-pipz)$_2$ (**XV**)	8.4(8.2)	56.8(57.0)	5.2(5.0)	11.6(11.8)	Brown	5.01
$Co(2\text{-}O_2NC_6H_4COO)_2$(1,4$Me_2$-pipz) (**XVI**)	11.9(11.7)	47.7(47.5)	4.6(4.4)	10.8(11.1)	Bluish-violet	4.93
$Co(2\text{-}O_2NC_6H_4COO)_2$(2,6$Me_2$-pipz) (**XVII**)	11.4(11.7)	46.8(47.5)	4.6(4.4)	10.7(11.1)	Light pink	4.82
$Co(2\text{-}O_2NC_6H_4COO)_2$(2,5$Me_2$-pipz) (**XVIII**)	11.2(11.7)	47.3(47.5)	4.6(4.4)	10.8(11.1)	Brown	4.72
$Co(2\text{-}O_2NC_6H_4COO)_2$(4Me-morl) (**XIX**)	12.2(12.0)	46.2(46.3)	4.1(3.8)	8.8(8.5)	Blue–violet	4.72
$Co(2\text{-}O_2NC_6H_4COO)_2$(3Me-pipd)$_2$ (**XX**)	10.1(10.0)	52.6(53.0)	5.7(5.8)	9.4(9.5)	Reddish-violet	4.67
$Co(2\text{-}O_2NC_6H_4COO)_2$(4Me-pipd)$_2$ (**XXI**)	9.9(10.0)	52.4(53.0)	5.9(5.8)	9.2(9.5)	Brown	4.61
$Co(3\text{-}O_2NC_6H_4COO)_2$(pipz) (**XXII**)	12.1(12.4)	44.9(45.3)	3.9(5.8)	11.6(11.7)	Light violet	4.84
$Co(3\text{-}O_2NC_6H_4COO)_2$(1Me-pipz)$_2 \cdot 2H_2O$ (**XXIII**)	9.2(9.4)	45.5(45.9)	5.7(5.7)	13.6(13.4)	Reddish-brown	4.79
$Co(3\text{-}O_2NC_6H_4COO)_2$(1Ph-pipz)$_2$ (**XXIV**)	8.2(8.2)	56.8(57.1)	5.2(5.0)	11.9(11.8)	Brown	4.79
$Co(3\text{-}O_2NC_6H_4COO)_2$(2Me-pipz) (**XXV**)	11.8(12.0)	46.6(46.4)	4.2(4.1)	11.6(11.4)	Bluish-pink	4.65
$Co(3\text{-}O_2NC_6H_4COO)_2$(1,4$Me_2$-pipz) (**XXVI**)	11.6(11.7)	47.2(47.5)	4.4(4.4)	10.8(11.1)	Blue	4.82
$Co(3\text{-}O_2NC_6H_4COO)_2$(2,6$Me_2$-pipz) (**XXVII**)	10.9(11.7)	47.2(47.5)	4.5(4.4)	11.2(11.1)	Light pink	4.75
$Co(3\text{-}O_2NC_6H_4COO)_2$(2,5$Me_2$-pipz) (**XXVIII**)	11.4(11.7)	47.2(47.5)	4.4(4.4)	11.0(11.1)	Light brown	4.61
$Co(3\text{-}O_2NC_6H_4COO)_2$(4Me-morl) (**XXIX**)	12.1(12.0)	46.2(46.3)	4.1(3.9)	8.2(8.5)	Blue	4.95
$Co(3\text{-}O_2NC_6H_4COO)_2$(2Me-pipd) (**XXX**)	12.1(12.0)	48.5(49.0)	4.5(4.3)	8.4(8.6)	Green	4.64
$Co(3\text{-}O_2NC_6H_4COO)_2$(3Me-pipd)$_2$ (**XXXI**)	10.2(10.0)	52.7(53.0)	5.9(5.8)	9.4(9.5)	Brown	4.74
$Co(3\text{-}O_2NC_6H_4COO)_2$(4Me-pipd)$_2$ (**XXXII**)	10.0(10.0)	52.6(53.0)	6.0(5.7)	9.8(9.5)	Brown	4.69
$Ni(4\text{-}O_2NC_6H_4COO)_2$(pipz) (**XXXIII**)	12.0(12.4)	45.1(45.3)	3.9(3.8)	11.7(11.7)	Light green	3.25
$Ni(4\text{-}O_2NC_6H_4COO)_2$(1Me-pipz)$_2 \cdot 2H_2O$ (**XXXIV**)	9.2(9.4)	46.0(45.9)	5.9(5.7)	13.6(13.4)	Light green	3.14
$Ni(4\text{-}O_2NC_6H_4COO)_2$(2Me-pipz) (**XXXV**)	11.8(12.0)	46.3(46.4)	4.2(4.1)	11.5(11.4)	Light green	3.08
$Ni(4\text{-}O_2NC_6H_4COO)_2$(1Ph-pipz)$_2$ (**XXXVI**)	8.0(8.2)	57.2(57.0)	5.2(5.0)	11.6(11.7)	Yellow	3.08

Ni(4-$O_2NC_6H_4COO)_2$(1,4Me_2-pipz) **(XXXVII)**	11.7(11.7)	47.6(47.5)	4.5(4.4)	10.8(11.1)	Green	3.22
Ni(4-$O_2NC_6H_4COO)_2$(2,6Me_2-pipz) **(XXXVIII)**	11.4(11.7)	47.2(47.5)	4.2(4.4)	10.8(11.1)	Light green	3.10
Ni(4-$O_2NC_6H_4COO)_2$(2,5Me_2-pipz) **(XXXIX)**	11.5(11.7)	47.6(47.5)	4.5(4.4)	11.2(11.1)	Yellowish-green	3.00
Ni(4-$O_2NC_6H_4COO)_2$(4Me-morl) **(XL)**	11.8(12.0)	46.3(46.3)	4.1(3.9)	8.5(8.5)	Light yellow	3.27
Ni(4-$O_2NC_6H_4COO)_2$(3Me-pipd)$_2$ **(XLI)**	10.0(10.0)	52.6(53.0)	5.8(5.8)	9.3(9.5)	Green	3.20
Ni(4-$O_2NC_6H_4COO)_2$(4Me-pipd)$_2$ **(XLII)**	9.7(10.0)	52.6(53.0)	5.9(5.8)	9.3(9.5)	Green	2.93
Ni(2-$O_2NC_6H_4COO)_2$(pipz) **(XLIII)**	12.1(12.3)	44.9(45.3)	3.9(3.8)	11.9(11.7)	Light green	3.09
Ni(2-$O_2NC_6H_4COO)_2$(1Me-pipz)$_2 \cdot 2H_2O$ **(XLIV)**	9.3(9.4)	45.3(45.9)	5.9(5.7)	13.6(13.4)	Light green	3.24
Ni(2-$O_2NC_6H_4COO)_2$(2Me-pipz) **(XLV)**	11.9(12.0)	46.2(46.4)	4.3(4.1)	11.9(11.4)	Light green	2.96
Ni(2-$O_2NC_6H_4COO)_2$(1Ph-pipz)$_2$ **(XLVI)**	8.1(8.2)	56.8(57.1)	5.2(5.0)	11.8(11.7)	Yellowish-green	3.03
Ni(2-$O_2NC_6H_4COO)_2$(1,4Me_2-pipz) **XLVII)**	11.5(11.7)	47.8(47.5)	4.5(4.4)	10.9(11.1)	Green	3.12
Ni(2-$O_2NC_6H_4COO)_2$(2,6Me_2-pipz) **(XLVIII)**	11.5(11.7)	47.3(47.5)	4.5(4.4)	10.9(11.1)	Light green	3.16
Ni(2-$O_2NC_6H_4COO)_2$(2,5Me_2-pipz) **(XLIX)**	11.6(11.7)	47.4(47.5)	4.3(4.4)	10.8(11.1)	Green	3.16
Ni(2-$O_2NC_6H_4COO)_2$(4Me-morl) **(L)**	11.7(12.0)	46.3(46.3)	4.0(3.9)	8.6(8.6)	Green	3.27
Ni(2-$O_2NC_6H_4COO)_2$(3Me-pipd)$_2$ **(LI)**	10.0(10.0)	53.1(53.0)	5.9(5.8)	9.4(9.5)	Green	3.26
Ni(2-$O_2NC_6H_4COO)_2$(4Me-pipd)$_2$ **(LII)**	9.8(10.0)	52.9(53.0)	5.9(5.8)	9.4(9.5)	Green	2.95
Ni(3-$O_2NC_6H_4COO)_2$(pipz) **(LIII)**	12.1(12.4)	45.3(45.3)	3.9(3.8)	11.9(11.8)	Light green	3.00
Ni(3-$O_2NC_6H_4COO)_2$(1Me-pipz)$_2 \cdot 2H_2O$ **(LIV)**	9.2(9.4)	45.8(45.9)	5.9(5.7)	13.6(13.4)	Yellowish-green	3.07
Ni(3-$O_2NC_6H_4COO)_2$(1Ph-pipz)$_2$ **(LV)**	8.2(8.3)	57.1(57.1)	5.1(5.0)	12.1(11.8)	Yellowish-green	3.07
Ni(3-$O_2NC_6H_4COO)_2$(2Me-pipz) **(LVI)**	11.9(12.0)	46.5(46.4)	4.2(4.1)	11.3(11.4)	Light green	2.96
Ni(3-$O_2NC_6H_4COO)_2$(1,4Me_2-pipz) **(LVII)**	11.5(11.7)	47.6(47.5)	4.4(4.4)	11.2(11.1)	Light green	3.14
Ni(3-$O_2NC_6H_4COO)_2$(2,6Me_2-pipz) **(LVIII)**	11.6(11.7)	47.7(47.5)	4.6(4.4)	11.1(11.1)	Light green	3.02
Ni(3-$O_2NC_6H_4COO)_2$(2,5Me_2-pipz) **(LIX)**	11.4(11.7)	47.2(47.5)	4.5(4.4)	11.2(11.1)	Light green	3.12
Ni(3-$O_2NC_6H_4COO)_2$(4Me-morl) **(LX)**	12.2(12.0)	45.6(46.4)	3.7(3.9)	8.7(8.5)	Flesh coloured	3.26
Ni(3-$O_2NC_6H_4COO)_2$(3Me-pipd)$_2$ **(LXI)**	10.1(10.0)	52.9(53.0)	5.8(5.8)	9.9(9.6)	Green	3.27
Ni(3-$O_2NC_6H_4COO)_2$(4Me-pipd)$_2$ **(LXII)**	9.8(10.0)	52.8(53.0)	5.9(5.8)	9.5(9.6)	Green	3.07
Cu$(C_6H_5COO)_2$(pipz) **(LXIII)**	15.9(16.2)	54.9(55.2)	5.3(5.1)	7.2(7.2)	Blue	1.78
Cu$(C_6H_5COO)_2$(1Ph-pipz)$_2$ **(LXIV)**	10.2(10.1)	64.5(64.8)	6.1(6.0)	8.9(8.9)	Blue	1.77
Cu$(C_6H_5COO)_2$(2Me-pipz) **(LXV)**	15.5(15.7)	56.0(57.2)	5.6(5.4)	7.1(6.9)	Blue	1.77
Cu$(C_6H_5COO)_2$(2,6Me_2-pipz) **(LXVI)**	14.9(15.1)	57.0(57.2)	5.9(5.7)	6.7(6.7)	Light violet	1.78
Cu$(C_6H_5COO)_2$(2,5Me_2-pipz) **(LXVII)**	15.1(15.1)	56.9(57.2)	5.7(5.7)	6.6(6.7)	Blue	1.91
Cu$(C_6H_5COO)_2$(2Me-pipd)$_2$ **(LXVIII)**	12.5(12.6)	61.7(62.0)	7.1(7.2)	5.5(5.6)	Blue	1.86
Cu$(C_6H_5COO)_2$(3Me-pipd)$_2$ **(LXIX)**	12.7(12.6)	61.7(62.0)	7.0(7.2)	5.4(5.6)	Blue	1.88
Cu$(C_6H_5COO)_2$(4Me-pipd)$_2$ **(LXX)**	12.6(12.6)	61.6(62.0)	6.9(7.2)	5.6(5.6)	Blue	2.06
Cu(4-$O_2NC_6H_4COO)_2$(pipz) **(LXXI)**	13.0(13.2)	44.9(44.9)	3.7(3.7)	11.7(11.6)	Light violet	1.88
Cu(4-$O_2NC_6H_4COO)_2$(2Me-pipz) **(LXXII)**	12.7(12.8)	45.9(46.0)	4.1(4.0)	11.2(11.3)	Blue	1.83
Cu(4-$O_2NC_6H_4COO)_2$(1,4Me_2-pipz) **(LXXIII)**	12.4(12.5)	47.1(47.1)	4.4(4.3)	11.1(11.0)	Blue	1.87
Cu(4-$O_2NC_6H_4COO)_2$(2,6Me_2-pipz) **(LXXIV)**	12.4(12.5)	47.0(47.1)	4.5(4.3)	11.1(11.0)	Violet	1.90
Cu(4-$O_2NC_6H_4COO)_2$(2,5Me_2-pipz) **(LXXV)**	12.3(12.7)	47.2(47.1)	4.4(4.3)	10.9(11.0)	Light violet	1.77
Cu(4-$O_2NC_6H_4COO)_2$(1Me-pipz)$_2$ **(LXXVI)**	10.6(10.7)	47.9(48.4)	5.5(5.4)	13.9(14.1)	Light violet	1.87

Table 1—*continued*

Complex	M	C	H	N	Colour	μ_{eff}
$Cu(4\text{-}O_2NC_6H_4COO)_2(2Me\text{-}pipd)_2$ **(LXXVII)**	10.6(10.7)	52.8(52.6)	5.8(5.7)	9.2(9.4)	Light violet	1.89
$Cu(4\text{-}O_2NC_6H_4COO)_2(3Me\text{-}pipd)_2$ **(LXXVIII)**	10.6(10.7)	52.4(52.6)	5.7(5.7)	9.4(9.4)	Light violet	1.82
$Cu(4\text{-}O_2NC_6H_4COO)_2(4Me\text{-}pipd)_2$ **(LXXIX)**	10.6(10.7)	52.6(52.6)	5.8(5.7)	9.3(9.4)	Light violet	1.79
$Cu(2\text{-}O_2NC_6H_4COO)_2(pipz)$ **(LXXX)**	13.2(13.2)	44.7(44.9)	3.8(3.7)	11.6(11.6)	Sky blue	1.78
$Cu(2\text{-}O_2NC_6H_4COO)_2(2Me\text{-}pipz)$ **(LXXXI)**	12.7(12.8)	46.1(46.0)	3.9(4.0)	11.4(11.3)	Dark green	1.82
$Cu(2\text{-}O_2NC_6H_4COO)_2(1Ph\text{-}pipz)_2$ **(LXXXII)**	8.8(8.6)	56.8(56.7)	5.1(5.0)	11.6(11.7)	Light blue	1.88
$Cu(2\text{-}O_2NC_6H_4COO)_2(2,6Me_2\text{-}pipz)$ **(LXXXIII)**	12.6(12.5)	47.0(47.1)	4.4(4.3)	11.1(11.0)	Violet	1.79
$Cu(2\text{-}O_2NC_6H_4COO)_2(2,5Me_2\text{-}pipz)$ **(LXXXIV)**	12.4(12.5)	47.0(47.1)	4.2(4.3)	11.2(11.0)	Blue	1.78
$Cu(2\text{-}O_2NC_6H_4COO)_2(2Me\text{-}pipd)_2$ **(LXXXV)**	10.7(10.7)	52.3(52.6)	5.7(5.7)	9.4(9.4)	Blue	1.84
$Cu(2\text{-}O_2NC_6H_4COO)_2(4Me\text{-}pipd)_2$ **(LXXXVI)**	10.6(10.7)	52.7(52.6)	5.8(5.7)	9.5(9.4)	Blue	1.89
$Cu(2\text{-}O_2NC_6H_4COO)_2(3Me\text{-}pipd)_2$ **(LXXXVII)**	10.6(10.7)	52.7(52.6)	5.8(5.7)	9.9(9.4)	Light violet	2.01
$Cu(3\text{-}O_2NC_6H_4COO)_2(pipz)$ **(LXXXVIII)**	13.0(13.2)	44.7(44.9)	3.8(3.7)	11.7(11.6)	Blue	1.78
$Cu(3\text{-}O_2NC_6H_4COO)_2(2Me\text{-}pipz)$ **(LXXXIX)**	12.7(12.8)	45.8(46.0)	4.1(4.0)	11.2(11.3)	Blue	1.79
$Cu(3\text{-}O_2NC_6H_4COO)_2(1Ph\text{-}pipz)_2$ **(XC)**	8.6(8.6)	56.8(56.7)	5.0(5.0)	11.7(11.7)	Green	1.79
$Cu(3\text{-}O_2NC_6H_4COO)_2(1Me\text{-}pipz)_2$ **(XCI)**	10.4(10.7)	47.5(48.4)	5.4(5.4)	13.7(14.1)	Dark green	1.82
$Cu(3\text{-}O_2NC_6H_4COO)_2(2,6Me_2\text{-}pipz)$ **(XCII)**	12.4(12.5)	46.9(47.1)	4.4(4.3)	11.0(11.0)	Blue	1.93
$Cu(3\text{-}O_2NC_6H_4COO)_2(2,5Me_2\text{-}pipz)$ **(XCIII)**	12.3(12.5)	46.9(47.1)	4.2(4.3)	11.1(11.0)	Light blue	2.16
$Cu(3\text{-}O_2NC_6H_4COO)_2(2Me\text{-}pipd)_2$ **(XCIV)**	10.6(10.7)	52.4(52.6)	5.8(5.7)	9.4(9.4)	Blue	1.84
$Cu(3\text{-}O_2NC_6H_4COO)_2(3Me\text{-}pipd)_2$ **(XCV)**	10.7(10.7)	53.2(52.6)	5.8(5.7)	9.3(9.4)	Blue	1.81
$Cu(3\text{-}O_2NC_6H_4COO)_2(4Me\text{-}pipd)_2$ **(XCVI)**	10.6(10.7)	52.4(52.6)	5.7(5.7)	9.4(9.4)	Green	1.78
$Cu(C_6H_5COO)_2(pipz)_{0.5}$ **(XCVII)**	18.1(18.2)	55.4(55.1)	4.4(4.3)	3.9(4.0)	Green	1.56
$Cu(C_6H_5COO)_2(1Me\text{-}pipz)_{0.5}$ **(XCVIII)**	18.0(17.9)	55.5(55.7)	4.6(4.5)	4.0(3.9)	Green	1.47
$Cu(C_6H_5COO)_2(1Ph\text{-}pipz)$ **(XCIX)**	13.6(13.6)	61.8(61.6)	5.1(5.1)	6.1(6.0)	Green	1.53
$Cu(C_6H_5COO)_2(1Ph\text{-}pipz)_{0.5}$ **(C)**	16.3(16.4)	58.6(59.0)	4.5(4.5)	3.7(3.6)	Green	1.41
$Cu(C_6H_5COO)_2(1,4Me_2\text{-}pipz)_{0.5}$ **(CI)**	17.6(17.5)	56.3(56.3)	4.7(4.7)	3.9(3.9)	Green	1.47
$Cu(C_6H_5COO)_2(4Me\text{-}morl)$ **(CII)**	15.6(15.6)	55.8(56.1)	5.2(5.2)	3.5(3.4)	Green	1.41
$Cu(4\text{-}O_2NC_6H_4COO)_2(1Ph\text{-}pipz)$ **(CIII)**	11.2(11.4)	51.9(51.7)	3.8(3.9)	10.1(10.0)	Green	1.51
$Cu(4\text{-}O_2NC_6H_5COO)_2(1Ph\text{-}pipz)_{0.5}$ **(CIV)**	12.9(13.3)	47.6(47.8)	3.2(3.1)	8.9(8.8)	Green	1.48
$Cu(4\text{-}O_2NC_6H_4COO)_2(4Me\text{-}morl)$ **(CV)**	12.7(12.8)	46.0(45.9)	3.9(3.8)	8.5(8.5)	Green	1.51
$Cu(2\text{-}O_2NC_6H_4COO)_2(1,4Me_2\text{-}pipz)_{0.05}$ **(CVI)**	13.8(14.0)	44.9(45.0)	3.4(3.3)	9.1(9.3)	Green	1.53
$Cu(2\text{-}O_2NC_6H_4COO)_2(1Me\text{-}pipz)$ **(CVII)**	12.9(12.8)	46.0(46.0)	4.1(4.0)	11.1(11.3)	Green	1.49
$Cu(2\text{-}O_2NC_6H_4COO)_2(1Ph\text{-}pipz)$ **(CVIII)**	11.4(11.4)	51.7(51.7)	4.1(4.0)	10.2(10.0)	Green	1.53
$Cu(2\text{-}O_2NC_6H_4COO)_2(4Me\text{-}morl)$ **(CIX)**	12.7(12.8)	46.0(45.9)	3.9(3.8)	8.5(8.5)	Green	1.52
$Cu(3\text{-}O_2NC_6H_4COO)_2(1,4Me_2\text{-}pipz)_{0.5}$ **(CX)**	13.9(14.0)	45.1(45.1)	3.4(3.3)	9.4(9.3)	Light green	1.42
$Cu(3\text{-}O_2NC_6H_4COO)_2(4Me\text{-}morl)$ **(CXI)**	12.7(12.8)	45.7(45.9)	3.9(3.8)	8.3(8.6)	Green	1.49

[a] Calculated values are given in parentheses.

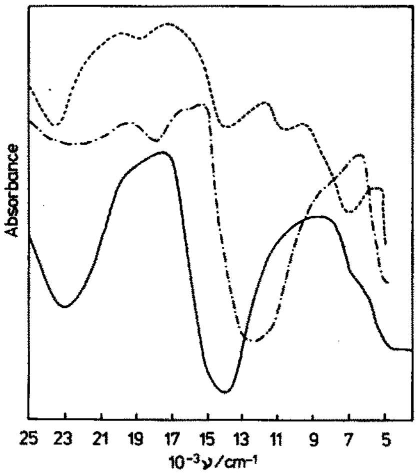


Fig. 1. Electronic reflectance spectra of $Co(4\text{-}O_2NC_6H_4COO)_2(3Me\text{-}pipd)_2$ (———), $Co(3\text{-}O_2NC_6H_4COO)_2(2Me\text{-}pipd)$ (–·–·–·), and $Co(2\text{-}O_2NC_6H_4COO)_2(4Me\text{-}morl)$ (– – – –).

$^3T_{1g}(F) \leftarrow {}^3A_{2g}(\nu_2)$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(\nu_3)$ transitions.[8,18,27] The ν_2 band is quite broad or is split into two components which can be ascribed to the large difference in the ligand-field strengths of the ligands in the present situation.[29] The low and high energy components of the ν_1 band can be assigned to the $^3B_{2g} \leftarrow {}^3B_{1g}(\nu_B)$ and $^3E_g \leftarrow {}^3B_{1g}(\nu_E)$ ligand-field transitions for the nickel(II) ion in D_{4h} environments.[8,29] Tetragonal parameters $Dq(xy)$, $Dq(z)$ and Dt, calculated from the energies of the above transitions, fall in the approximate ranges of 700, 1000 and -200 cm^{-1}, respectively. The position of the ν_3 band lies above 25,000 cm^{-1} for all complexes except the four complexes, i.e. $Ni(RCOO)_2(4Me\text{-}morl)$ (where R = 2-, 3-, and $4\text{-}O_2NH_4$) and $Ni(2\text{-}O_2NC_6H_4COO)_2(2,6Me_2\text{-}pipz)$, which exhibit this band at a much lower energy—around 21,000 cm^{-1}. It makes it a little doubtful to be considered as a ν_3 absorption of octahedral geometry. The value of Dq for most of the complexes, as calculated from the ratio ν_3/ν_1 or ν_3/ν_2, lies around 900 cm^{-1}, while the value of B shows variation between 800 and 1100 cm^{-1}. These results are in agreement with earlier reports on similar complexes of pseudo-octahedral geometry.[8,18,28] However, the B value for the four complexes having anomalous spectra comes out to be very small (550 cm^{-1}), which contradicts approximate octahedral structure (D_{4h} symmetry). However, we suggest a heavily distorted octahedral structure with C_{4v} symmetry for these complexes.

All magnetically dilute copper(II) complexes (**LXIII–XCVI** as in Table 1) under discussion show an electronic absorption band in the region 14,700–18,200 cm^{-1} which can be assigned to the $^2T_{2g} \leftarrow {}^2E_g$ ligand-field transition for an octahedral field. The broadness or splitting observed for this main band is ascribed to tetragonal distortion. The lower and higher energy components of this can be assigned, respectively, to the $^2B_{2g} \leftarrow {}^2B_{1g}$ (or $d_{xy} \rightarrow d_{x^2-y^2}$) and $^2E_g \leftarrow {}^2B_{1g}$ (or $d_{xz,yz} \rightarrow d_{x^2-y^2}$) ligand-field transitions for a tetragonal field.[30–32]

Two absorptions, one as a broad band in the region 12,500–14,500 cm^{-1} (band I) and the other as a shoulder around 26,000 cm^{-1} (band II), are observed for antiferromagnetic copper(II) complexes (**XCVIII–CXI**). Band I may be due to the absorption corresponding to the $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz,yz} \rightarrow d_{x^2y^2}$ electronic transitions for the copper(II) ion in tetragonal environments,[33] while band II can be assigned to the $2p_\pi$ (donor oxygen atom) $\rightarrow d_{x^2-y^2}$ charge-transfer transition. The appearance of this band is considered to be characteristic of the dimeric structure for the copper(II) carboxylate complexes.[33–35]

The X-band EPR curves of powdered materials for most of the magnetically dilute copper(II) complexes obtained at liquid nitrogen temperature are consistent with axial symmetry of the complexes except for $[Cu(C_6H_5\text{-}COO)_3(3Me\text{-}pipd)_2]$ which has an EPR spectrum typical of elongated rhombic geometry [g_z (2.33) $> g_y$(2.07) $> g_x$(2.05)]. The magnitudes $g_\parallel$ (2.20–2.27) and $g_\perp$ (2.05–2.09) obtained from the EPR spectrum for these complexes are consistent ($g_\parallel > g_\perp > 2.04$) with an elongated tetragonal type structure, which agrees with the results obtained from electronic absorption studies.[31,32] The observed range of $g_\parallel$ is in conformity with the CuO_4N_2 chromophore of the complex.[36] The absorptions for the $g_\parallel$ and g_z portions of the EPR spectra for $Cu(4\text{-}O_2NC_6H_4COO)_2(3Me\text{-}pipd)_2$ and $Cu(C_6H_5COO)_2(3Me\text{-}pipd)_2$, respectively, resolve into four components. The splitting is attributed to the hyperfine coupling due to ^{63}Cu ($I = 3/2$). The values of $A_\parallel = 0.0181$ cm^{-1} and $A_z = 0.0141$ cm^{-1} have been obtained, respectively, for these two complexes. The bonding parameters, $\alpha^2 = 0.829$, $\beta_1^2 = 0.854$ and $\beta^2 = 0.723$, have also been calculated for $Cu(4\text{-}O_2NC_6H_4COO)_2(3Me\text{-}pipd)_2$ by assuming D_{4h} symmetry for the copper(II) environments.[31,37,38]

The X-band EPR spectra at 300 K for powdered samples of antiferromagnetic complexes under present discussion contain absorption lines at field strengths of 800 (H_{z1}), 4600 ($H_\perp$) and 6100 G (H_{z2}), which are characteristic features of axially symmetric binuclear copper(II) species and correspond to the spin triplet state ($S = 1$) with $D > h\nu$ and $E = 0$.[39,40] The range of $g_\parallel$ or g_z (2.30–2.40), $g_\perp$ (2.05–2.10) and D (0.34–0.39 cm^{-1}) evaluated from the EPR spectra are comparable with the earlier reported values for binuclear copper(II) carboxylate complexes.[4–7] For some complexes, the EPR absorption around 800 G is split into seven lines due to hyperfine coupling of the nuclear spins of two copper ions with the electron spin ($2nI+1$; $n = 2$ and $I = 3/2$ for ^{63}Cu). The value of $A_{\parallel}$ or A_z is found to be about half ($\simeq 0.008$ cm^{-1}) of that generally observed for magnetically dilute copper(II) in similar environments. This supports magnetic exchange taking place between two metal ions.[40,41] However, in addition to the above-mentioned absorptions, an absorption line around 3200 G is also observed. The intensity of this line increases while the intensity of the lines due to the triplet state, as expected, decreases with the lowering of temperature. This line is, therefore, attributed to the magnetically dilute copper(II) impurity which is commonly present in the copper(II) arylcarboxylate complexes.[39,42,43]

Magnetic susceptibility studies

The room-temperature μ_{eff} values for all cobalt(II) complexes lie in the range 4.60–5.02, which is considerably greater than the spin-only value (3.82) and hence supports nearly octahedral structure for these complexes.[8,18,27] The magnitude of μ_{eff} varies with A (ligand-field strength parameter), k (covalence parameter for the M—L bond) and v (parameter for distortion from cubic symmetry).[44,45] For perfectly octahedral systems ($v = 0$) with $A = 1.4$ ($A = 1.4$ for complexes under discussion as calculated from electronic spectra) and $k = 0.8$ (minimum possible value for nature of ligands), the theoretical μ_{eff} value at room temperature for the complexes under discussion should be 4.81 or greater.[44] But in the present case, for most of the complexes μ_{eff} is less than 4.81, which leaves the distortion from cubic symmetry to be the only reason responsible for the lowering of the μ_{eff} values. The magnetic susceptibility of six representative cobalt(II) complexes, viz. $Co(4\text{-}O_2NC_6H_4COO)_2(1Ph\text{-}pipz)_2$ (**V**), $Co(4\text{-}O_2NC_6H_4COO)_2(3Me\text{-}pipd)_2$ (**X**), $Co(2\text{-}O_2NC_6H_4COO)_2(1,4Me_2\text{-}pipz)_2$ (**XVI**), $Co(2\text{-}O_2NC_6H_4COO)_2(4Me\text{-}morl)$ (**XIX**), $Co(3\text{-}O_2NC_6H_4COO)_2(pipz)$ (**XXII**) and $Co(3\text{-}O_2NC_6H_4COO)_2(1,4Me_2\text{-}pipz)$ (**XXVI**) has also been measured at different temperatures in the range 80–280 K. The magnitude of θ (10–54°) obtained from the plots of $1/\chi$ vs T, and the variation of μ_{eff} from 4.90 at 280 K to 4.2 at 80 K, which remains well above the spin-only value (except **XIX**), favours the $^4T_{1g}$ ground ligand-field term for these complexes with near octahedral structures.[45] The value of θ for the complex $Co(2\text{-}O_2NC_6H_4COO)_2(4Me\text{-}morl)$ (**XIX**) is 110° and this large value can only be due to antiferromagnetic interactions. The magnetic moment value of this complex decreases rapidly with a decrease in temperature, i.e. it decreases from 4.55 BM at 280 K to 3.4 BM at 80 K, which becomes even less than the spin-only value for high-spin cobalt(II) complex. These observations clearly indicate the presence of antiferromagnetic interactions taking place in this complex.[5]

The room-temperature μ_{eff} value for nickel(II) complexes under present discussion lies in the range 3.00–3.35. These values are consistent with the near octahedral structure for these complexes. Room-temperature magnetic moment values for the copper(II) complexes **LXIII–XCVI** and **XCVII–CXI** lie in the ranges 1.81–2.20 BM and 1.40–1.60 BM, respectively. In view of the μ_{eff} value for the former complexes lying above the spin-only value and for the latter being close to the value reported for dinuclear or polynuclear complexes, where carboxylate group acts as a bridge between two metal ions, the copper(II) complexes have been categorized as (i) magnetically dilute and (ii) antiferromagnetic complexes.[1–7]

Antiferromagnetic copper(II) complexes have also been characterized by magnetic susceptibility measurements at different temperatures.[15] The magnetic moment value for all these complexes decreases with temperature, thus confirming their antiferromagnetic behaviour. The following modified equation based upon Bleaney and Bowers' model[46] was employed to evaluate the spin-exchange parameter ($-2J$) from magnetic susceptibility data at different temperatures:[42,43]

$$\ln\left[\frac{N\bar{g}^2\beta^2(1-x)}{kT\left(\chi_{\text{Cu}}-\dfrac{0.43x}{T}-N_\alpha\right)}-3\right]=\frac{-2J}{kT}$$

$$\text{or}\quad \ln(F-3)=\frac{-2J}{kT}.$$

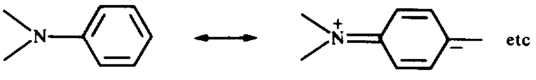
The unknown quantities in the above expression on the LHS were as follows: the value of $\bar{g}$ was determined from EPR measurements and the value of N_α was taken to be 60×10^{-6} e.g.s. units. The value of x, the mole fraction of paramagnetic impurity, was so chosen as to fit in well with the above expression. The value of $2J$ has been determined from the slope $[2J/k]$ of the straight line obtained from a plot of $\ln(F-3)$ vs $1/T$. The value of $2J$ was also calculated from the variation of intensity (I) of the EPR lines at the temperatures 300, 173 and 103 K using the relation:[39,43]

$$\frac{A_1}{A_2}=\frac{I_1}{I_2}=\frac{T_2(3+e^{-2J/kT_2})}{T_1(3+e^{-2J/kT_1})}.$$

The relative areas of curves $[A_1/A_2]$ at two different temperatures (T_1 and T_2) were estimated by the reported methods.[47,48] Uncertainties in the values of $-2J$ for the former and latter methods are ± 5 and ± 20 cm^{-1}, respectively. This is because both of these methods have their own limitations in evaluating the value of $2J$. The magnetic susceptibility method becomes complicated due to the presence of a magnetically dilute impurity which is usually present in antiferromagnetic copper(II) arylcarboxylate complexes. However, by allowing the presence of this impurity (x) in the above equation, reasonable evaluation of $2J$ can be obtained. The EPR method, though it is free from the presence of the magnetic impurity, suffers from the limitation in evaluating the accurate areas under EPR curves. Therefore the uncertainties in the EPR method are greater than in the magnetic susceptibility method. The values of $-2J$ determined by the two methods are comparable and lie between 280–330 cm^{-1}.

In spite of the high basicities of these bases (p$K_a \simeq$ 8–9.6), this range of values of $2J$ is comparable to that for the earlier reported copper(II) carboxylate complexes with terminal ligands of low basicity, e.g. py, etc. No consistent trend of the variation of $-2J$ with pK_as of the acids or the ligand is obtained.

By combining all the studies conducted upon all these complexes, the distorted octahedral structure can be assigned to all complexes except for $Co(3\text{-}O_2NC_6H_4COO)_2$(2Me-pipd), $Co(2\text{-}O_2NC_6H_4COO)_2$(4Me-morl) and all antiferromagnetic copper(II) complexes (**XCVII–XCI**). The monomeric *trans*-pseudo-octahedral structure with the carboxylate group acting as a chelating bidentate unit and the base as a monodentate ligand has been assigned to the complexes of the type $M(RCOO)_2(L—L)_2 \cdot xH_2O$ and $M(RCOO)_2L_2$, where $x = 2$ for L—L = 1Me-pipz and $x = 0$ for L—L = 1Ph-pipz; and L = 2-, 3- or 4Me-pipd. Here, for the 1Me-pipz complexes, the two water molecules may be hydrogen bonded to the uncoordinated nitrogen atom, i.e. the $N—CH_3$ group of the base.[18] The absence of these water molecules in similar complexes of 1Ph-pipz may be attributed to the phenyl group using the lone pair of the uncoordinated nitrogen atom for delocalization (see below) and hence lessening the possibility of hydrogen bonding.



Leaving aside the antiferromagnetic complexes, the polymeric *trans*-pseudo-octahedral structure with the carboxylate group and the heterocyclic base acting, respectively, as a chelating bidentate and a bridging bidentate ligand between two metal atoms, has been assigned to all complexes of the type $M(RCOO)_2(L—L)$ except for $Ni(2\text{-}O_2NC_6H_4COO)_2(L—L)$ (where L—L = 2Me-pipz, 2,5Me$_2$-pipz, 1,4Me$_2$-pipz) and $Ni(3\text{-}O_2NC_6H_4COO)_2$(1,4-Me$_2$-pipz), for which the geometry with both L—L and the carboxylate group behaving as bridging bidentate groups is proposed. The trigonal bipyramidal structure has been suggested for $Co(3\text{-}O_2NC_6H_4COO)_2$(2Me-pipd). For antiferromagnetic complexes, the copper(II) acetate monohydrate-like dinuclear structure[49] for complexes of the type $M(RCOO)_2(L—L)$ and the $Cu(HCOO)_2(\text{dioxane})_{0.5}$-like polymeric structure[50] containing binuclear units for complexes of the type $Cu(RCOO)_2(L—L)_{0.5}$ are proposed.

Our interest in the present work was to study the complexation behaviour of these saturated mono- and diheterocyclic bases, of different but high basicities and different steric characteristics, with metal(II) carboxylates. An additional interest was to see whether these bases form magnetically dilute or antiferromagnetic complexes. Out of these cases, 4Me-morl and 1,4Me$_2$-pipz are interesting ligands. 4-Methylmorpholine forms only 1 : 1 complexes (when added in excess) with all copper(II) carboxylates of the type $Cu(RCOO)_2$ (where R = C_6H_5, 2-, 3- and 4-$O_2NC_6H_4$); all of them are found to be antiferromagnetic. Out of all the cobalt(II) and nickel(II) complexes, the only antiferromagnetic complex to be isolated was also that of 4Me-morl with the formula $Co(2\text{-}O_2NC_6H_4COO)_2$(4Me-morl). 1,4-Dimethylpiperazine forms complexes of the type $Cu(RCOO)_2(1,4Me_2\text{-pipz})_{0.5}$ (where R = C_6H_5, 2- and 3-$O_2NC_6H_4$ and when R = 4-$O_2NC_6H_4$) and for all the cobalt(II) and nickel(II) nitrobenzoates, it affords complexes of 1 : 1 stoichiometry. Complexes having 1 : 0.5 stoichiometry are antiferromagnetic, while those of 1 : 1 stoichiometry are magnetically dilute. The 1Me-pipz and 1Ph-pipz ligands form complexes of 1 : 2, 1 : 1 and 1 : 0.5 (metal–base) stoichiometry with copper(II) carboxylates, while with cobalt(II) and nickel(II) they give 1 : 2 complexes. The complexes of 1 : 2 stoichiometry are magnetically dilute while the others are antiferromagnetic. These bases are of interest for copper(II) carboxylates, where one can change the stoichiometry and structural form of the complex and hence its magnetic behaviour by controlling only the amount of base added to the metal carboxylate solution. All other diheterocyclic bases form complexes of 1 : 1 stoichiometry, which are found to be magnetically dilute. Overall, the complexation behaviour of these diheterocyclic bases can be rationalized to some extent by the following factors: (1) copper(II) carboxylates have more tendency to form antiferromagnetic complexes than their cobalt(II) and nickel(II) analogues; (2) bases with lower pK_a values and large steric hindrance (e.g. 4Me-morl and 1,4Me$_2$-pipz) prefer to form antiferromagnetic complexes.

Out of the monoheterocyclic bases, 2Me-pipd shows restricted complexation behaviour, compared with 3Me-pipd and 4Me-pipd, in its adduct formation with cobalt(II) and more so with nickel(II) nitrobenzoates, i.e. it does not form any adduct with nickel(II) nitrobenzoates and gives only 1 : 1 complexes with Co(RCOO)$_2$ (where R = 3- or 4-$O_2NC_6H_4$) and when R = 2-$O_2NC_6H_4$ a complex does not form; while its 3- and 4Me-pipd analogues give 1 : 2 complexes with all metal(II) carboxylates. These three bases behave similarly with copper(II) carboxylates to give 1 : 2 complexes. This can be partly justified due to the larger steric requirements of 2Me-pipd than the other ligands. The similarity in behaviour of the three bases for copper(II) may be due to large Jahn–Teller effects expected for copper(II) and especially its particular preferential mode, i.e. Jahn–Teller elongation which forces the complexes to adopt a *trans*–in-plane tetragonally elongated structure which results in relieving some steric congestion in the structure.[51,52] To some extent, this can also be justified by the larger affinity of the copper(II) ion than cobalt(II) and nickel(II) ions for complexation with highly basic nitrogen donors. These bases do not yield any antiferromagnetic complexes [not even with copper(II)], which can also be due to their highly basic nature.

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