| | |
|---|---|
| $V$ | molar volume |
| $x$ | mole fraction |

*Greek Letters*

| | |
|---|---|
| $\alpha$ | nonrandomness parameter |
| $\Gamma_{ji}$ | ratio defined by eq 7 |
| $\eta$ | shear viscosity |
| $\nu$ | kinematic viscosity |
| $\rho$ | density |
| $\xi$ | $\ln(\eta V)$ |
| $\sigma$ | free energy of activation parameter |
| $\theta$ | Hagenbach-Couette error correction factor |
| $\phi$ | volume fraction |
| $\phi_i^*$ | volume fraction at specific composition defined by eq 6 |
| $\phi_{ji}$ | local volume fraction of $j$ around component $i$ |

**Registry No.** Acetone, 67-64-1; carbon tetrachloride, 56-23-5; chloroform, 67-66-3; cyclohexane, 110-82-7; dimethyl sulfoxide, 67-68-5; ethanol, 64-17-5; hexane, 110-54-3; 2-propanol, 67-63-0; methanol, 67-56-1; methyl acetate, 79-20-9; propanol, 71-23-8; triethylamine, 121-44-8.

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# Excess Volumes of Benzene + 1-Hexanol and + 3-Methyl-3-pentanol at Three Different Temperatures

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**Excess volumes for benzene with 1-hexanol and 3-methyl-3-pentanol have been measured over the entire composition range at 298.15, 303.15, and 308.15 K. $V^E$ values were obtained with an oscillator type densimeter and the analytical expressions which represent the composition dependences of the excess volume are reported.**

Experimental excess properties are needed to relate and compute the properties of liquid mixtures and then to be compared with those derived from theoretical formalism of classical thermodynamics. Studies of the thermodynamic properties of pure alcohols and of their mixtures with other molecular species are very important because they may provide information about the variation of these properties with the number and positions of the hydroxyl group in the alcohol. The purpose of this investigation is to measure the excess volumes for two binary systems formed by benzene with 1-hexanol and 3-methyl-3-pentanol (3-M-3-P) from density values as a function of temperature between 298.15 and 308.15 K. Likewise, from excess volumes at those temperatures, the temperature coefficients of $V^E$ were calculated.

## Experimental Section

The benzene used was supplied by Carloerba with a stated purity of ≥99.5 mol %; however, 1-hexanol and 3-M-3-P were "puriss" grade from Fluka (AG) and their purity was ≥99.0 mol %. Both the benzene and the alcohols were used as received without further purification.

The physical properties of the pure liquids are compared with literature values in Table I. In general, agreement with them is satisfactory; however, there appear to exist no reliable recent measurements for 3-M-3-P.

All mixtures were prepared by weight on a Mettler H10 analytical balance. The probable error in the mole fraction is estimated to be less than $10^{-4}$. The densities $\rho$ were measured with a digital density meter DMA-55 (Anton Paar, KG, Graz, Austria) with a reproducibility of $\pm 0.00001$ g cm$^{-3}$. The apparatus was calibrated at each temperature with redistilled and degassed water and dry air at atmospheric pressure. The samples in the densimeter were thermostated by a Heto Birkeroad ultrathermostat, the temperature being controlled within ±0.01 K by a digital thermometer DT-100 (Anton Paar) with a thermistor calibrated previously.

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**Table I. Densities $\rho$ and Refractive Indices $n_D$ of Pure Substances at 298.15 K**

| | $\rho$, kg m$^{-3}$ | | $n_D$ | |
|---|---|---|---|---|
| | this work | lit. | this work | lit. |
| benzene | 873.51 | 873.7 (*1*), 873.67 (*4*), 873.63 (*6*) | 1.4980 | 1.49792 (*1*), 1.4979 (*6*), 1.49792 (*4*) |
| 1-hexanol | 815.10 | 815.9 (*1*), 815.1 (*3*), 815.91 (*5*) | 1.4156 | 1.4161 (*1*), 1.4157 (*3*), 1.41612 (*5*) |
| 3-M-3-P | 823.63 | 823.1 (*2*) | 1.4166 | 1.4192 (*2*) |

**Table II. Experimental Densities $\rho$ and Excess Volumes as a Function of Temperature**

| 298.15 K | | | 303.15 K | | | 308.15 K | | |
|---|---|---|---|---|---|---|---|---|
| $x$ | $\rho$, g cm$^{-3}$ | $V^E$, cm$^3$ mol$^{-1}$ | $x$ | $\rho$, g cm$^{-3}$ | $V^E$, cm$^3$ mol$^{-1}$ | $x$ | $\rho$, g cm$^{-3}$ | $V^E$, cm$^3$ mol$^{-1}$ |
| | | | $x\mathrm{C_6H_6} + (1-x)\mathrm{C_6H_{13}OH}$ | | | | | |
| 0.0000 | 0.815 10 | 0.0000 | 0.0000 | 0.811 51 | 0.0000 | 0.0000 | 0.807 92 | 0.0000 |
| 0.1075 | 0.819 02 | 0.1039 | 0.1082 | 0.815 42 | 0.0914 | 0.0993 | 0.811 29 | 0.0978 |
| 0.1410 | 0.820 42 | 0.1180 | 0.1377 | 0.816 49 | 0.1215 | 0.1404 | 0.812 70 | 0.1444 |
| 0.1725 | 0.821 67 | 0.1435 | 0.1708 | 0.817 75 | 0.1507 | 0.1748 | 0.814 08 | 0.1580 |
| 0.2268 | 0.823 97 | 0.1761 | 0.2316 | 0.820 16 | 0.1986 | 0.2320 | 0.816 33 | 0.1956 |
| 0.2577 | 0.825 27 | 0.2003 | 0.2617 | 0.821 51 | 0.2053 | 0.2606 | 0.817 48 | 0.2153 |
| 0.3081 | 0.827 47 | 0.2362 | 0.3106 | 0.823 63 | 0.2333 | 0.3035 | 0.819 21 | 0.2491 |
| 0.3380 | 0.828 89 | 0.2467 | 0.3419 | 0.825 00 | 0.2541 | 0.3380 | 0.820 75 | 0.2603 |
| 0.3852 | 0.831 16 | 0.2620 | 0.3948 | 0.827 47 | 0.2767 | 0.3905 | 0.823 04 | 0.2931 |
| 0.4205 | 0.832 92 | 0.2785 | 0.4210 | 0.828 74 | 0.2857 | 0.4213 | 0.824 51 | 0.3000 |
| 0.4513 | 0.834 50 | 0.2876 | 0.4479 | 0.829 99 | 0.3052 | 0.4528 | 0.825 95 | 0.3198 |
| 0.4759 | 0.835 75 | 0.2995 | 0.4645 | 0.830 84 | 0.3083 | 0.4786 | 0.827 24 | 0.3243 |
| 0.4960 | 0.836 84 | 0.3023 | 0.4998 | 0.832 64 | 0.3199 | 0.4991 | 0.828 20 | 0.3381 |
| 0.5858 | 0.841 87 | 0.3178 | 0.5857 | 0.837 36 | 0.3274 | 0.5838 | 0.832 62 | 0.3560 |
| 0.6489 | 0.845 66 | 0.3204 | 0.6523 | 0.841 30 | 0.3230 | 0.6403 | 0.835 83 | 0.3534 |
| 0.6630 | 0.846 57 | 0.3167 | 0.6620 | 0.841 89 | 0.3222 | 0.6621 | 0.837 10 | 0.3529 |
| 0.7335 | 0.851 22 | 0.3001 | 0.7337 | 0.846 46 | 0.3072 | 0.7289 | 0.841 27 | 0.3320 |
| 0.7872 | 0.855 11 | 0.2665 | 0.7849 | 0.850 03 | 0.2782 | 0.7890 | 0.845 30 | 0.3013 |
| 0.8492 | 0.859 85 | 0.2228 | 0.8523 | 0.855 07 | 0.2257 | 0.8566 | 0.850 31 | 0.2375 |
| 0.8651 | 0.861 10 | 0.2115 | 0.8644 | 0.856 05 | 0.2111 | 0.8669 | 0.851 07 | 0.2312 |
| 0.9395 | 0.867 47 | 0.1273 | 0.9360 | 0.861 95 | 0.1344 | 0.9340 | 0.856 58 | 0.1430 |
| 1.0000 | 0.873 51 | 0.0000 | 1.0000 | 0.868 15 | 0.0000 | 1.0000 | 0.862 83 | 0.0000 |
| | | | $x\mathrm{C_6H_6} + (1-x)\mathrm{C_2H_5CCH_3OHC_2H_5}$ | | | | | |
| 0.0000 | 0.830 69 | 0.0000 | 0.0000 | 0.826 21 | 0.0000 | 0.0000 | 0.821 68 | 0.0000 |
| 0.0976 | 0.832 29 | 0.2187 | 0.1080 | 0.827 83 | 0.2576 | 0.1026 | 0.823 20 | 0.2411 |
| 0.1323 | 0.832 96 | 0.2853 | 0.1425 | 0.828 57 | 0.3105 | 0.1387 | 0.823 78 | 0.3213 |
| 0.1663 | 0.833 83 | 0.3218 | 0.1688 | 0.829 13 | 0.3530 | 0.1556 | 0.824 18 | 0.3421 |
| 0.2401 | 0.835 61 | 0.4237 | 0.2196 | 0.830 29 | 0.4265 | 0.2252 | 0.825 66 | 0.4535 |
| 0.2589 | 0.835 99 | 0.4610 | 0.2658 | 0.831 36 | 0.4961 | 0.2624 | 0.826 51 | 0.5079 |
| 0.3116 | 0.837 49 | 0.5108 | 0.3041 | 0.832 33 | 0.5448 | 0.3002 | 0.827 54 | 0.5430 |
| 0.3312 | 0.837 97 | 0.5414 | 0.3304 | 0.833 08 | 0.5685 | 0.3286 | 0.828 23 | 0.5826 |
| 0.3812 | 0.839 47 | 0.5861 | 0.3736 | 0.834 40 | 0.5994 | 0.3818 | 0.829 76 | 0.6261 |
| 0.4027 | 0.840 26 | 0.5883 | 0.4137 | 0.835 67 | 0.6262 | 0.4161 | 0.830 75 | 0.6617 |
| 0.4420 | 0.841 54 | 0.6168 | 0.4435 | 0.836 63 | 0.6460 | 0.4467 | 0.831 74 | 0.6797 |
| 0.4692 | 0.842 50 | 0.6291 | 0.4662 | 0.837 41 | 0.6567 | 0.4638 | 0.832 29 | 0.6908 |
| 0.4986 | 0.843 55 | 0.6433 | 0.5013 | 0.838 67 | 0.6692 | 0.4943 | 0.833 34 | 0.7038 |
| 0.5839 | 0.846 96 | 0.6536 | 0.5791 | 0.841 65 | 0.6857 | 0.5781 | 0.836 52 | 0.7154 |
| 0.6528 | 0.849 96 | 0.6492 | 0.6304 | 0.843 89 | 0.6730 | 0.6478 | 0.839 46 | 0.7049 |
| 0.6566 | 0.850 16 | 0.6454 | 0.6649 | 0.845 40 | 0.6692 | 0.6565 | 0.839 88 | 0.6985 |
| 0.7253 | 0.853 59 | 0.6072 | 0.7246 | 0.848 40 | 0.6269 | 0.7307 | 0.843 54 | 0.6452 |
| 0.7737 | 0.856 39 | 0.5478 | 0.7864 | 0.851 89 | 0.5543 | 0.7893 | 0.846 72 | 0.5845 |
| 0.8347 | 0.860 03 | 0.4762 | 0.8300 | 0.854 47 | 0.5006 | 0.8457 | 0.850 19 | 0.4950 |
| 0.8568 | 0.861 49 | 0.4393 | 0.8635 | 0.856 61 | 0.4474 | 0.8720 | 0.851 88 | 0.4503 |
| 0.9326 | 0.867 03 | 0.2756 | 0.9363 | 0.861 99 | 0.2749 | 0.9315 | 0.856 29 | 0.2996 |
| 1.0000 | 0.873 51 | 0.0000 | 1.0000 | 0.868 15 | 0.0000 | 1.0000 | 0.862 83 | 0.0000 |

## Results

From densities of the pure components and the binary mixtures, the molar excess volumes are calculated by using

$$V^E = x_1M_1(\rho^{-1} - \rho_1^{-1}) + (1 - x_1)M_2(\rho^{-1} - \rho_2^{-1}) \quad (1)$$

where $M_1$ and $M_2$ denote the molar masses, $\rho_1$ and $\rho_2$ are the densities of the pure substances, $x_1$ is the mole fraction of benzene, and $\rho$ is the density of the mixture. The densities and excess volumes for benzene + 1-hexanol and + 3-M-3-P at 298.15, 303.15, and 308.15 K are summarized in Table II. Because of the proximity of the values of $V^E$ for the three temperatures, the representation of the experimental results and the fitting curves at each temperature mentioned above are presented in separate figures (Figures 1–3). For each mixture the excess volumes were fitted to a smoothing function already used by one of us in other papers (*7–9*)

$$V^E = C[Z(1 - Z)]^b \quad (2)$$

where $Z$ is related to the mole fraction through the expression

$$Z = x_1/\{x_1 + R(1 - x_1)\} \quad (3)$$

The parameters $R$, $C$, and $b$ were found by a nonlinear regression procedure using a HP-85 calculator. Essentially, given two fixed values for $R$ and $b$, the program evaluates, for the set values, the standard deviation, $\sigma(V^E)$. Then, $R$ is varied to reach the minimum of $\sigma(V^E)$ and finally one can vary $b$ until the absolute minimum of the standard deviation is found with respect to $b$ and $R$.

The parameters of eq 2 are included in Table III along with

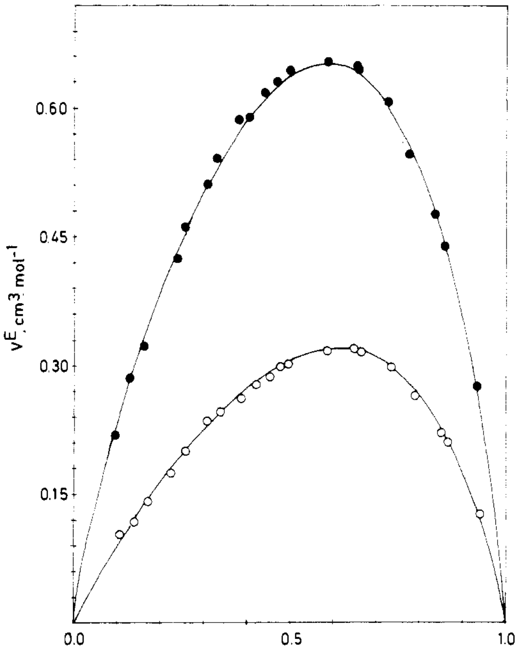

**Figure 1.** Excess volumes $V^E$ against the mole fraction of benzene at 298.15 K: (○) benzene + 1-hexanol; (●) benzene + 3-methyl-3-pentanol.

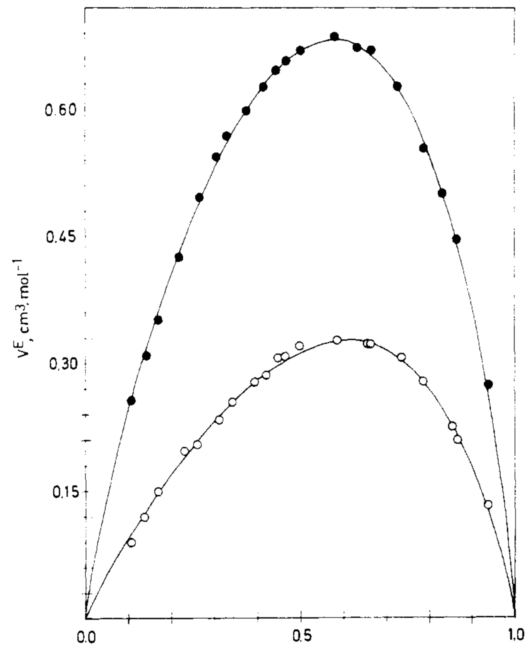

**Figure 2.** Excess volumes $V^E$ against the mole fraction of benzene at 303.15 K: (○) benzene + 1-hexanol; (●) benzene + 3-methyl-3-pentanol.

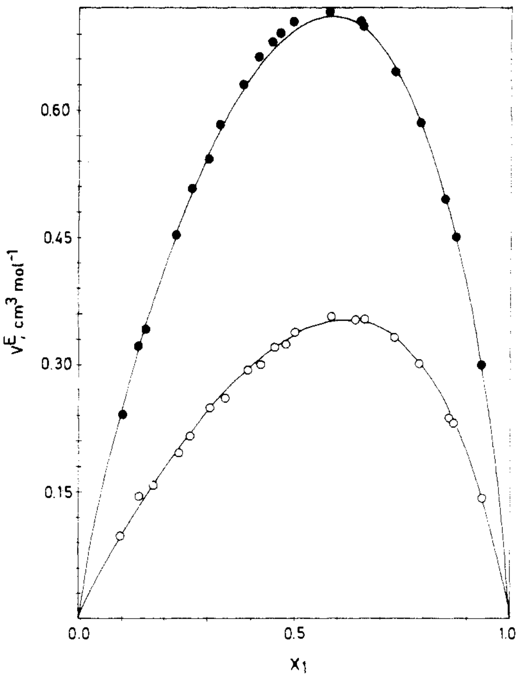

**Figure 3.** Excess volumes $V^E$ against the mole fraction of benzene at 308.15 K: (○) benzene + 1-hexanol; (●) benzene + 3-methyl-3-pentanol.

**Table III. Parameters of Eq 2 and the Standard Deviations $\sigma(V^E)$**

| $T$, K | $C$, cm$^3$ mol$^{-1}$ | $R$ | $b$ | $\sigma(V^E)$, cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|
| | $x$C$_6$H$_6$ + (1 − $x$)1-Hexanol | | | |
| 298.15 | 1.1161 | 1.566 | 0.90 | 0.0042 |
| 303.15 | 1.1405 | 1.550 | 0.90 | 0.0046 |
| 308.15 | 1.2265 | 1.600 | 0.90 | 0.0046 |
| | $x$C$_6$H$_6$ + (1 − $x$)3-M-3-P | | | |
| 298.15 | 1.9775 | 1.402 | 0.80 | 0.0073 |
| 303.15 | 2.0684 | 1.364 | 0.80 | 0.0058 |
| 308.15 | 2.1528 | 1.388 | 0.80 | 0.0072 |

the standard deviation $\sigma(R^E)$, which is evaluated from the equation

$$\sigma(V^E) = [\sum(V^E - V^E_{\text{calcd}})^2/N]^{1/2} \qquad (4)$$

where $N$ is the number of experimental points.

The values of $V^E$ for the binary mixtures studied are positive over the entire range of compositions at all temperatures. Excess volumes of benzene + 1-hexanol have been investigated previously; however, the results present in the literature do not exhibit much accuracy. Recently values of $V^E$ for this mixture were obtained by Myers and Clever (*10*) at 303.15 K, which are slightly higher than ours—with a maximum deviation of 0.05 cm$^3$ mol$^{-1}$ in the proximity of $x_1$ = 0.75 (mole fraction of benzene).

The excess volume-composition curves are slightly deflected to the richer benzene region for all system and at the three temperatures, showing an absolute maximum value in the proximity of $x_1$ = 0.61 for the benzene + 1-hexanol mixtures and of $x_1$ = 0.58 for benzene + 3-M-3-P systems. From a simplified model presented by Brown, Fock, and Smith (*11*), the changes in the thermodynamic functions which appear on mixing an alcohol with benzene are due to the strong interaction between the hydroxyl group and benzene with the breaking of hydrogen bonds and also to the interactions of the alcohol homomorphs with the benzene by effect of mixing. A survey of Table II data shows that $V^E$ for the benzenes + 3-M-3-P system are higher than those for the 1-hexanol + benzene one. From these results we should then expect the experimental excess volumes of mixing for the other hexanol isomers to decrease in the order tertiary > secondary > primary, a rule which can be established because of the different range of the interaction between the homomorph of the alcohol and the solvent.

The excess volumes of these systems increase with increasing temperature from 298.15 to 308.15 K as might be expected from the discussion of the authors mentioned above (ref *11*). The values of $(\partial V^E/\partial T)_p$ for the systems studied here are all positive and at $x_1$ = 0.5 range between 0.0029 and 0.0057 cm$^3$ mol$^{-1}$ K$^{-1}$ for the systems benzene + 1-hexanol and benzene + 3-M-3-P, respectively. It is observed that the excess volumes vary linearly with temperature over nearly the whole range of composition; the results of $(\partial V^E/\partial T)_p$ present asymmetrical curves vs. the composition with a maximum value of 0.0023 $cm^3\ mol^{-1}\ K^{-1}$ near $x_1 = 0.6$ for benzene + 1-hexanol and 0.0058 $cm^3\ mol^{-1}\ K^{-1}$ near $x_1 = 0.6$ for benzene + 3-M-3-P mixtures.

**Registry No.** 3-M-3-P, 77-74-7; benzene, 71-43-2; 1-hexanol, 111-27-3.

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# NEW COMPOUNDS

## Magnetic and Spectral Studies of *S*-Benzyl-*N*-phenylthiocarbamoylthiobenzamide Complexes with Some Bivalent Metal Ions

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**The complexes with chemical compositions $VOL_2SO_4$, $ML_2Cl_2$ [M = Cu(II), Cd(II), Hg(II)], and $M'(L-H)_2$ [M′ = Cu(II), Co(II), Ni(II)], L = *S*-benzyl-*N*-phenylthiocarbamoylthiobenzamide, $PhC(SCH_2Ph){=}NC({=}S)NHPh$ (BPTT, L), have been prepared and characterized by analytical data, molar conductance, molecular weight, magnetic susceptibility, electronic, infrared, ESR, and X-ray powder diffraction studies. The complexes have been screened for antifungal activity.**

### Introduction

Metal complexes of sulfur donor ligands have received great attention recently (*1*) due to their versatile use as pesticides (*2*) and fungicides (*3*, *4*). The toxicological importance of the –N–C–S– moiety has been well established in a number of fungicides and pesticides (*5*). The complete absence of previous work on transition-metal complexes of BPTT and the possibility of these complexes having antifungal activity prompted us to undertake synthesis and structural studies of $V^{II}O$, Co(II), Ni(II), Cu(II), Cd(II), and Hg(II) complexes of the above ligand.

### Experimental Section

***Materials.*** All the chemicals used in the present study were of British Drug House (BDH) or equivalent grade. The ligand was prepared following the procedure described earlier (*6*).

***Synthesis of the Complexes.*** The complexes $VOL_2SO_4$ and $ML_2Cl_2$ were prepared by adding a methanolic/ethanolic solution of metal salt to the acetone solution of the ligand in 1:2 molar ratio. All the complexes precipitated almost immediately except $VOL_2SO_4$, which was obtained by heating the reaction mixture on a water bath for a few minutes and keeping it overnight.

The deprotonated complexes, $M'(L-H)_2$, were synthesized by mixing ethanolic solutions of appropriate metal acetate and ligand in 1:2 molar ratio with constant stirring. The resulting complexes were digested on a water bath for $^1/_2$ h to ensure complete deprotonation.

The complexes thus obtained were suction filtered and repeatedly washed with water (in the case of deprotonated complexes only), with ethanol/methanol to remove unreacted metal salt and ligand (if any), and then with ether and finally dried in vacuo.

***Analysis of the Complexes.*** The complexes were analyzed for metal content by standard procedure (*7*). The chloride and sulfur were determined gravimetrically as AgCl and $BaSO_4$, respectively, and nitrogen was determined microanalytically. The analytical data are given in Table I.

***Physical Measurements.*** Molar conductance of the complexes in DMF at $10^{-3}$ M concentration was determined at room temperature on a WTW conductivity meter. The molecular weight of $VOL_2SO_4$, $Co(L-H)_2$, $Ni(L-H)_2$, and $Cu(L-H)_2$ was determined cryoscopically by using nitrobenzene as solvent and that of other complexes could not be determined due to their insolubility. Magnetic susceptibility of the complexes was measured at room temperature on a Cahn–Faraday electrobalance by using $HgCo(NCS)_4$ as calibrant and was corrected for diamagnetism (*8*). The molar conductance, molecular weight, and magnetic moment data are included in Table I. The UV and visible spectra of the ligand and the complexes in Nujol were recorded on a Cary-14 spectrophotometer while IR spectra of the ligand and the complexes were recorded on a Perkin-Elmer spectrophotometer Model 621 in Nujol (4000–200 $cm^{-1}$) and in KBr (4000–400 $cm^{-1}$). The electronic spectral