h. The organic solution was separated from the mixture and dried (K_2CO_3). Evaporation of the solution gave desired complexes, which were precipitated from toluene–hexane as dark solids.

Other Chemicals. PhCN from commercial origin was refluxed on P_2O_5 for 24 h and distilled before use. NBu_4ClO_4 and NBu_4Cl (Fluka purum) were recrystallized twice from acetone–water mixtures and dried under reduced pressure at 50 °C. $HClO_4$ solutions in PhCN were prepared from 70% aqueous perchloric acid (Prolabo).

Cyclic Voltammetry and Spectroelectrochemistry. The instrumentation, cells, and electrodes for cyclic voltammetry and thin-layer spectroelectrochemistry were the same as previously described.[9a] In the spectrophotometric experiments, preelectrolyzed solutions of the Fe^{II} complexes were used the electrolysis was carried out in a coulometric cell with a graphite working electrode, a platinum-wire counterelectrode, and a NaCl SCE reference electrode.

The determination of $K^{II}{}_A$ for e-(C12)$_2$-CT–Fe^{II}OH, a-(C12)$_2$-CT–Fe^{II} OH and a-(C12)$_2$-CT–Fe^{II}Cl derived from the variations of the UV–vis spectrum with concentration (C) according to the following procedure. Let α be the dissociation coefficient of the complex:

$$\alpha = [(1 + 4K^{II}{}_AC)^{1/2} - 1]/2K^{II}{}_AC$$

At a given C, the observed extinction coefficient, α, is given by

$$\epsilon - \epsilon_1 = (\epsilon_2 - \epsilon_1)(1 - \alpha)$$

where ϵ_1 and ϵ_2 are the extinction coefficients of the [Fe^{II}] and [Fe^{II}OH]$^-$ complex at the same wavelength. ϵ_1 is known from the spectrum of the neutralized solution. As shown in Figures 4 and 5, the experimental log $|\epsilon - \epsilon_1|$ vs. log C plot is fitted with the log $(1 - \alpha)$ vs. log $(K^{II}{}_AC)$ working curve by sliding of both the horizontal and vertical axis. The coincidence of the experimental and theoretical horizontal scales gives the value of $K^{II}{}_A$, and the coincidence of the vertical scales gives ϵ_2. The range of concentration was selected so as to obtain a range of α values sufficiently different from 0 and 1.

Registry No. [e-(C12)$_2$-CT–Fe^{III}]$^+$, 93646-90-3; e-(C12)$_2$-CT–Fe^{II}, 70196-65-5; [e-(C12)$_2$-CT–Fe^{I}]$^-$, 79209-91-9; e-(C12)$_2$-CT–Fe^{III}OH, 93646-91-4; [e-(C12)$_2$-CT–Fe^{II}OH]$^-$, 93646-92-5; e-(C12)$_2$-CT–Fe^{III}Cl, 79198-03-1; [e-(C12)$_2$-CT–Fe^{II}Cl]$^-$, 90837-98-2; [a-(C12)$_2$-CT–Fe^{III}]$^+$, 93646-93-6; a-(C12)$_2$-CT–Fe^{II}, 93646-94-7; [a-(C12)$_2$-CT–Fe^{I}]$^-$, 90838-20-3; [a-(C12)$_2$-CT–Fe^{0}]$^{2-}$, 90838-23-6; a-(C12)$_2$-CT–Fe^{III}OH, 93646-95-8; [a-(C12)$_2$-CT–Fe^{II}OH]$^-$, 93646-96-9; a-(C12)$_2$-CT–Fe^{III}Cl, 90838-12-3; [a-(C12)$_2$-CT–Fe^{II}Cl]$^-$, 90838-14-5; K_2CO_3, 584-08-7.

Contribution from the Departments of Chemistry, University of Wollongong, Wollongong, N.S.W., Australia 2500, and University of Virginia, Charlottesville, Virginia 22901

Copper(II) and Nickel(II) Complexes of Unsymmetrical Tetradentate Schiff Base Ligands

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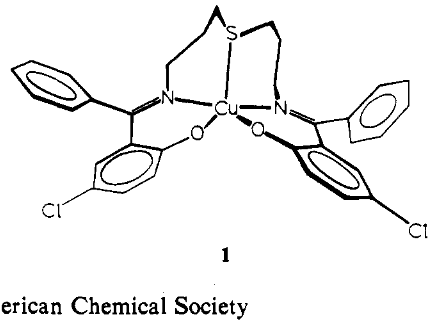
Received March 27, 1984

A systematic synthesis is described for new types of unsymmetrical tetradentate Schiff base ligands, from the condensation of different aldehydes and ketones with the two amino groups of 1,2-diaminobenzene. 5-Chloro-2-hydroxybenzophenone (HCBP), dissolved in methanol, reacts with one amino group of 1,2-diaminobenzene to form a tridentate Schiff base ligand (HCBP-PHEN). The free amino group of this ligand can then be reacted with a series of substituted salicylaldehydes (XSALH) to form unsymmetrical tetradentate Schiff base ligands (HCBP-PHEN-XSALH). These ligands react with copper(II) and nickel(II) acetates to form complexes of the type M(CBP-PHEN-XSAL). The physicochemical properties of a series of these complexes have been measured. The crystal structures of three of the copper complexes have been determined. Crystal data for [Cu(CBP-PHEN-SAL)]·CH_3OH: space group $P\bar{1}$, $Z = 2$, $a = 8.666$ (4) Å, $b = 10.061$ (4) Å, $c = 14.104$ (8) Å, $\alpha = 103.01$ (3)°, $\beta = 104.38$ (4)°, $\gamma = 93.07$ (2)°, $V = 1153$ Å^3, $R = 5.5\%$ for 2259 reflections. Crystal data for [Cu(CBP-PHEN-5-ClSAL)]·H_2O: space group $P2_1/c$, $Z = 4$, $a = 15.296$ (6) Å, $b = 7.166$ (2) Å, $c = 25.288$ (6) Å, $\beta = 107.68$ (3)°, $V = 2641$ Å^3, $R = 6.9\%$ for 1220 reflections. Crystal data for [Cu(CBP-PHEN-5-OCH_3SAL)]·CH_3OH: space group $P\bar{1}$, $Z = 2$, $a = 8.973$ (3) Å, $b = 10.148$ (9) Å, $c = 15.836$ (5) Å, $\alpha = 98.80$ (4)°, $\beta = 118.35$ (3)°, $\gamma = 95.18$ (5)°, $V = 1232$ Å^3, $R = 6.4\%$ for 1875 reflections. A 2-mol portion of 5-chloro-2-hydroxybenzophenone, in the absence of solvent, reacts, on refluxing, with 1 mol of 1,2-diaminobenzene to form the symmetrical tetradentate Schiff base ligand HCBP-PHEN-HCBP. The nickel(II) complex of this ligand has been prepared and its crystal structure determined. Crystal data for [Ni(CBP-PHEN-CBP)]: space group $P\bar{1}$, $Z = 2$, $a = 8.516$ (3) Å, $b = 10.783$ (3) Å, $c = 13.057$ (3) Å, $\alpha = 78.82$ (4)°, $\beta = 80.40$ (4)°, $\gamma = 86.28$ (2) °, $V = 1295$ Å^3, $R = 5.6\%$ for 2510 reflections. [Cu(CBP-PHEN-Im)] differs from its analogue in that it is hindered from forming the CuO_2Cu bridge with metal salts and hexafluoroacetylacetonate (hfa) complexes. However, it can still form adducts via imidazole bridging, and its adducts with Cu(hfa)$_2$ and Co(hfa)$_2$ were formed to demonstrate this.

Introduction

Transition metals occur in metalloenzymes[2–5] bound to a macrocycle such as a heme ring or to donor atoms of peptide chains usually in a distorted environment, as in hemerythrin[4] (Fe$_2$) or hemocyanin[5] (Cu$_2$). Symmetric tetradentate Schiff base (TSB) complexes of cobalt(II) have been used extensively as macrocycle models, while asymmetric complexes are required to model the irregular binding of peptides. Asymmetric complexes can be produced by distorting the planar geometry of M(TSB) complexes with the addition of a weak fifth donor atom such as S or O in **1**[6,7] or by incomplete Schiff base condensation as in **2**.[8] Alter-



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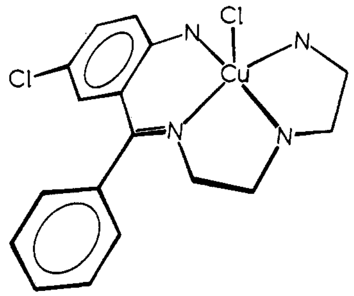
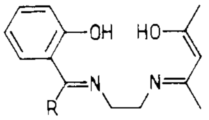


2

natively, unsymmetrical ligands such as **3** with Cu(II),[9] Ni(II),[10] and Pd(II),[10] **4** with Cu(II)[11] and Ni(II),[11,12] and **5**[13] and **6**[14] with Cu(II) and Ni(II) should produce distorted metal environments. However, no crystal structures have been reported; the amount of distortion from planar geometry is not known. We report here the physical and structural properties of the Cu(II) and Ni(II) complexes of the asymmetrical ligands, **7**, derived from the stepwise condensation of 1,2-diaminobenzene with 5-chloro-2-hydroxybenzophenone, and then with another aldehyde such as salicylaldehyde, pyrrole-2-carbaldehyde, or imidazole-4-carbaldehyde.



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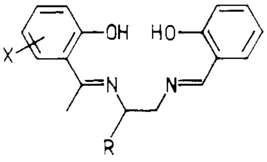

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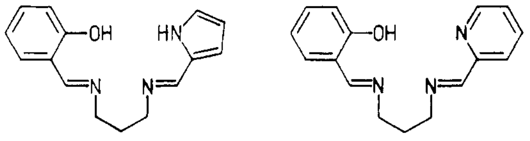

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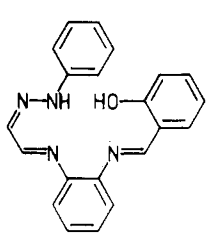

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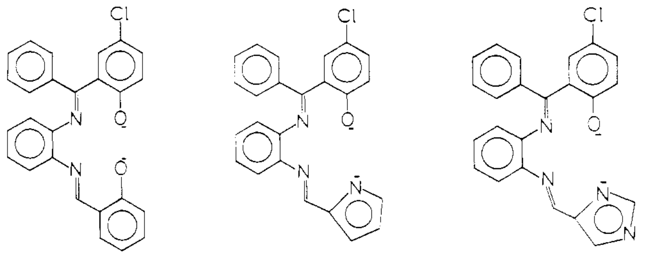

7

Experimental Section

Starting materials were obtained from Aldrich Chemical Co. and Pfaltz and Bauer, Inc.

5-Chloro-2-hydroxybenzophenone (HCBP) was prepared by a modified version of the method described by Hayashi.[15] Anhydrous aluminum chloride (133 g, 1 mol) was placed in a 2-L round-bottom flask and heated to about 50 °C. Benzoyl chloride (141 g, 1 mol) was added to the flask. 4-Chlorophenol (130 g, 1 mol) was added, in portions of about 15 g, to the reaction mixture, which rapidly became hot, evolving fumes of HCl. The flask was then heated to 180 °C for 40 min and then allowed to cool to room temperature; hydrochloric acid (5%, 1.5 L) was then poured into the flask that was then allowed to stand for 24 h. The hydrochloric acid was then decanted from the flask, and the yellow solid was washed twice with water. The HCBP was then recrystallized from hot methanol and recrystallized a second time from hot methanol containing activated charcoal. The compound was obtained as yellow crystals: mp 93–94 °C, lit.[15] mp 95 °C; yield 180 g.

HCBP-PHEN. 5-Chloro-2-hydroxybenzophenone 40 g, 0.17 mol), 1,2-diaminobenzene (18.5 g, 0.17 mol), piperidine (15 g, 0.18 mol), and triethylorthoformate (20 mL) were refluxed in absolute ethanol (150 mL) until the orange crystalline product started to precipitate from solution. The solution was allowed to cool to room temperature, and the product was collected by filtration: mp 192 °C; yield 35 g.

HCBP-PHEN-XSALH. HCBP-PHEN (30 g, 0.06 mol) was suspended in hot methanol (100 mL). The appropriate substituted salicylaldehyde (0.065 mol) was added to the suspension, and piperidine (0.1 mol) was then added to the mixture. The mixture was then boiled until the product precipitated from solution. The solution was then allowed to cool to room temperature and the product collected by filtration; yield 80–95%.

HCBP-PHEN-PYRRH. HCBP-PHEN (20 g, 0.06 mol), pyrrole-2-carbaldehyde (6.2 g, 0.065 mol), and piperidine (8.5 g, 0.1 mol) were refluxed in methanol (150 mL) unitl all the reactants had dissolved. The solution was then filtered and used for the preparation of the metal complexes.

4(5)-Formylimidazole. 4(5)-(Hydroxymethyl)imidazole hydrochloride was prepared from imidazol-4-yl methoxyhydroxypicrate.[16] The hydrochloride salt was converted to the free base by neutralization with Na$_2$CO$_3$. The neutral alcohol was oxidized to the aldehyde by the action of manganese dioxide in dioxane at 80 °C.[17]

HCBP-PHEN-4-Im. HCBP-PHEN (0.17 g, 0.52 mmol) and 4(5)-formylimidazole (0.09 g, 0.52 mmol) were refluxed in methanol for 30 min. The resulting solution of the Schiff base was used for the preparation of the metal complex.

HCBP-PHEN-HCBP. HCBP-PHEN (10 g, 0.03 mol) and 5-chloro-2-hydroxybenzophenone (7.2 g, 0.03 mol) were refluxed, without solvent, for 30 min. The resulting melt solidified to a glassy solid, on cooling, and was dissolved in hot 1-butanol (100 mL), filtered, and used for the preparation of the nickel complex.

Metal Complexes. (1) ML. (a) General Method. HCBP-PHEN-XSALH (0.01 mol) was dissolved in the minimum quantity of hot 1-butanol containing piperidine (0.01 mol). This solution was then added

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to a hot filtered solution of the metal acetate (0.01 mol) in methanol (200 mL). The resulting solution was boiled until the complex precipitated.

(b) M(CBP-PHEN-4,6-MeO$_2$SAL). The synthesis was carried out as described in method a except that dichloromethane was used as the ligand's solvent due to its poor solubility in 1-butanol.

(c) M(CBP-PHEN-PYRR). The ligand was not isolated from its preparation solution; instead, it was reacted immediately with the metal acetate in methanol. Apart from this, the preparation method was the same as that described in method a using the ligand preparation solution.

Cu(CBP-PHEN-Im)M(hfa)$_2$. Binuclear complexes were prepared by the reaction of Cu(CBP-PHEN-Im), prepared as in method c, with $M(CF_3\cdot CO\cdot CH\cdot CO\cdot CF_3)_2$ (M(hfa)$_2$: M = Cu, Co). The reaction was carried out in a 1/1 fashion in a 50/50 dichloromethane–butanol solvent system. The use of butanol was required to precipitate out the binuclear product. Both adducts were isolated as deep red microcrystalline solids, and both were characterized by FAB mass spectroscopy as well as microanalysis.

(d) Ni(CBP-PHEN-CBP). Method a was followed, making use of the ligand preparation solution. The resulting product was a mixture of Ni(CBP-PHEN-CBP) and Ni(CBP-PHEN)$_2$. This mixture was heated in dichloromethane and filtered. The filtrate contained Ni(CBP-PHEN-CBP), and the residue was impure Ni(CBP-PHEN)$_2$. Methanol was added to the filtrate and the solution allowed to evaporate unitl the complex precipitated from solution.

(2) NiL(py)$_2$. Ni(CBP-PHEN-SAL) (2 g) was dissolved in the minimum quantity of hot pyridine and the solution filtered and allowed to evaporate until the adduct precipitated.

Physical Measurements. (1) Analyses. Carbon, hydrogen, and nitrogen analyses (Tables I and II) were carried out by AMDEL Microanalytical Service, Victoria, Australia.

(2) Visible and Near-Infrared Spectra. Solid-state spectra (Nujol mull) and solution spectra were measured on a Cary 17 spectrophotometer.

(3) Magnetic Moments. Room-temperature magnetic moments were measured by the Gouy method. FAB (fast atom bombardment) mass spectrometry was carried out as previously described.[18]

(4) X-ray Crystallography. Crystal Data and Data Collection. [Cu(CBP-PHEN-SAL)]·CH$_3$OH: $CuClO_3N_2C_{27}H_{21}$, mol wt 520, space group $P\bar{1}$, $Z = 2$, $a = 8.666$ (4) Å, $b = 10.061$ (4) Å, $c = 14.104$ (8) Å, $\alpha = 103.01$ (3)°, $\beta = 104.38$ (4)°, $\gamma = 93.07$ (2)°, $V = 1153$ Å^3, $\rho_{calcd} = 1.50$ g cm^{-3}, $\rho_{obsd} = 1.48$ g cm^{-3}, μ(Mo Kα) = 11.2 cm^{-1}; crystal dimensions (distances in mm of faces from centroid) (100) 0.12, $(\bar{1}00)$ 0.12, (010) 0.11, $(0\bar{1}0)$ 0.11, (001) 0.08, $(00\bar{1})$ 0.08; maximum, minimum transmission coefficients 0.98, 0.91.

[Cu(CBP-PHEN-5-ClSAL)]·H$_2$O: $CuCl_2O_3N_2C_{26}H_{18}$, mol wt 575, space group $P2_1/c$, $Z = 4$, $a = 15.296$ (6) Å, $b = 7.166$ (2) Å, $c = 25.288$ (6) Å, $\beta = 107.68$ (3)°, $V = 2641$ Å^3, $\rho_{calcd} = 1.44$ g cm^{-3}, $\rho_{obsd} = 1.41$ g cm^{-3}, μ(Mo Kα) = 10.0 cm^{-1}; crystal dimensions (mm from centroid) (100) 0.10, $(\bar{1}00)$ 0.10, (010) 0.06, $(0\bar{1}0)$ 0.06, (001) 0.09, $(00\bar{1})$ 0.09; maximum, minimum transmission coefficients 0.94, 0.91.

[Cu(CBP-PHEN-5-OCH$_3$SAL)]·CH$_3$OH: $CuClO_4N_2C_{27}H_{24}$, mol wt 535, space group $P\bar{1}$, $Z = 2$, $a = 8.973$ (3) Å, $b = 10.148$ (9) Å, $c = 15.836$ (5) Å, $\alpha = 98.80$ (4)°, $\beta = 118.35$ (3)°, $\gamma = 95.18$ (5)°, $V = 1232$ Å^3, $\rho_{calcd} = 1.44$ g cm^{-3}, $\rho_{obsd} = 1.40$ g cm^{-3} μ(Mo Kα) = 9.3 cm^{-1}; crystal dimensions (mm from centroid) (100) 0.28, $(\bar{1}00)$ 0.28, (010) 0.28, $(0\bar{1}0)$ 0.28, (001) 0.06, $(00\bar{1})$ 0.06, $(1\bar{1}\bar{1})$ 0.20, $(\bar{1}11)$ 0.20; maximum, minimum transmission coefficients 0.95, 0.77.

[Ni(CBP-PHEN-CBP)]: $NiCl_2O_2N_2C_{32}H_{20}$, mol wt 594, space group $P\bar{1}$, $Z = 2$, $a = 8.516$ (3) Å, $b = 10.783$ (3) Å, $c = 13.057$ (3) Å, $\alpha = 78.82$ (4)°, $\beta = 80.40$ (4)°, $\gamma = 86.28$ (2)°, $V = 1295$ Å^3, $\rho_{calcd} = 1.52$ g cm^{-3}, $\rho_{obsc} = 1.50$ g cm^{-3}, μ(Mo, Kα) = 9.9 cm^{-1}; crystal dimensions (mm from centroid) (101) 0.11, $(\bar{1}0\bar{1})$ 0.11, $(10\bar{1})$ 0.27, $(\bar{1}01)$ 0.27, (010) 0.04, $(0\bar{1}0)$ 0.04; maximum, minimum transmission coefficients 0.95, 0.88.

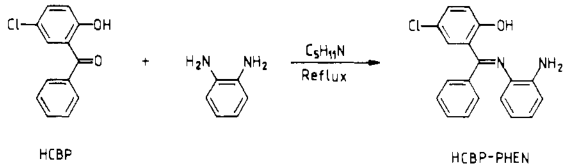
Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ–2θ scan technique was used, as previously described,[19] to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 48°$ for [Cu(CBP-PHEN-SAL)]·CH$_3$OH and [Cu(CBP-PHEN-5-OCH$_3$SAL)]·CH$_3$OH, $1° < 2\theta < 47°$ for [Cu(CBP-PHEN-5-ClSAL)]·H$_2$O, and $1° < 2\theta < 49°$ for [Ni(CBP-PHEN-CBP)]. Scan widths were calculated as $(A + B \tan \theta)$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.70 and 0.35°, respectively, for [Cu(CBP-PHEN-SAL)]·CH$_3$OH and 0.60 and 0.35°, respectively, for the other three complexes.

The intensities of four standard reflections were monitored for each crystal at 100 reflection intervals and showed no greater fluctuations than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and absorption. Of the 2799 independent intensities for [Cu(CBP-PHEN-SAL)]·CH$_3$OH, 2491 for [Cu(CBP-PHEN-5-ClSAL)]·H$_2$O, 2097 for [Cu(CBP-PHEN-5-OCH$_3$SAL)]·CH$_3$OH, and 3490 for [Ni(CBP-PHEN-CBP)], there were 2259, 1220, 1875, and 2510 for the four complexes respectively with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[20] These data were used in the final refinement of the structural parameters.

Structure Determinations. In each case, the position of the metal atoms was determined from three-dimensional Patterson functions. The intensity data were phased sufficiently well by these positional coordinates to permit location of the other non-hydrogen atoms from Fourier difference syntheses. Full-matrix least-squares refinement was carried out as previously described.[19] In each case, anisotropic temperature factors were introduced for all non-hydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinements for three cycles of least squares and then held fixed. The models converged with $R = 5.5\%$, $R_w = 6.6\%$ for [Cu(CBP-PHEN-SAL)]·CH$_3$OH, $R = 6.9\%$, $R_w = 7.6\%$ for [Cu(CBP-PHEN-5-ClSAL)]·H$_2$O, $R = 6.4\%$, $R_w = 6.9\%$ for [Cu(CBP-PHEN-5-OCH$_3$SAL)]·CH$_3$OH, and $R = 5.6\%$, $R_w = 6.3\%$ for [Ni(CBP-PHEN-CBP)]. Final Fourier difference functions were featureless. Tables of the observed and calculated structure factors are available[21] together with least-squares planes and microanalytical data. The principal programs are as previously described.[19]

Results and Discussion

Ligands. When 5-chloro-2-hydroxybenzophenone reacts in methanol with 1,2-diaminobenzene, in the presence of piperidine, Schiff base condensation occurs at only one of the two available amino groups, even in the presence of a large excess of ketone (eq 1). This contrasts with the behavior of salicylaldehyde, which condenses with both amino groups under similar conditions. From space-filling models, there is no obvious steric reason for the lack of condensation at the second amino group. When the reaction is carried out in the absence of solvent, condensation does occur at both amine groups (eq 2). If therefore appears that the first Schiff base condensation so deactivates the second amino group that it will only react with 5-chloro-2-hydroxybenzophenone under more severe conditions. This free amino group of HCBP-PHEN is sufficiently reactive to condense with substituted salicylaldehydes, as well as other appropriate aldehydes and ketones, to form unsymmetrical Schiff base ligands (eq 3 and 4).



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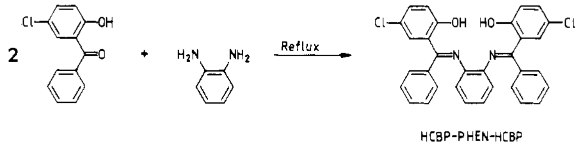

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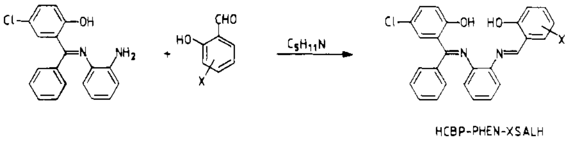

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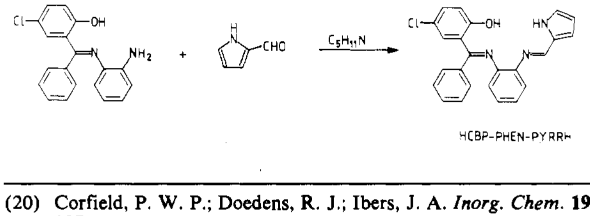

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[21] Supplementary material.

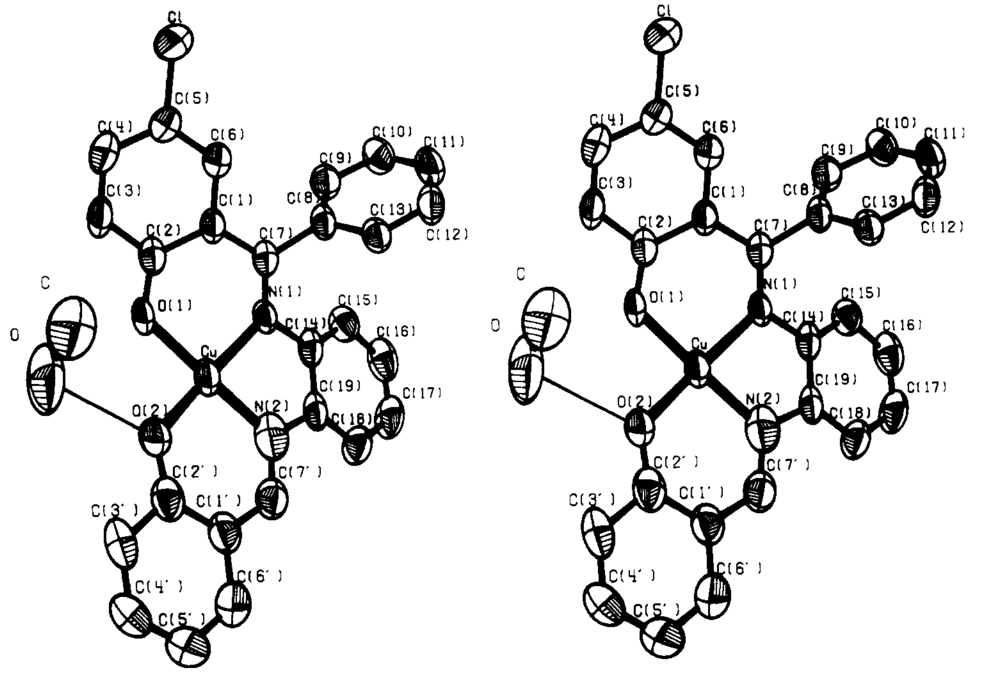

Figure 1. Stereoview of [Cu(CBP-PHEN-SAL)]·CH_3OH.

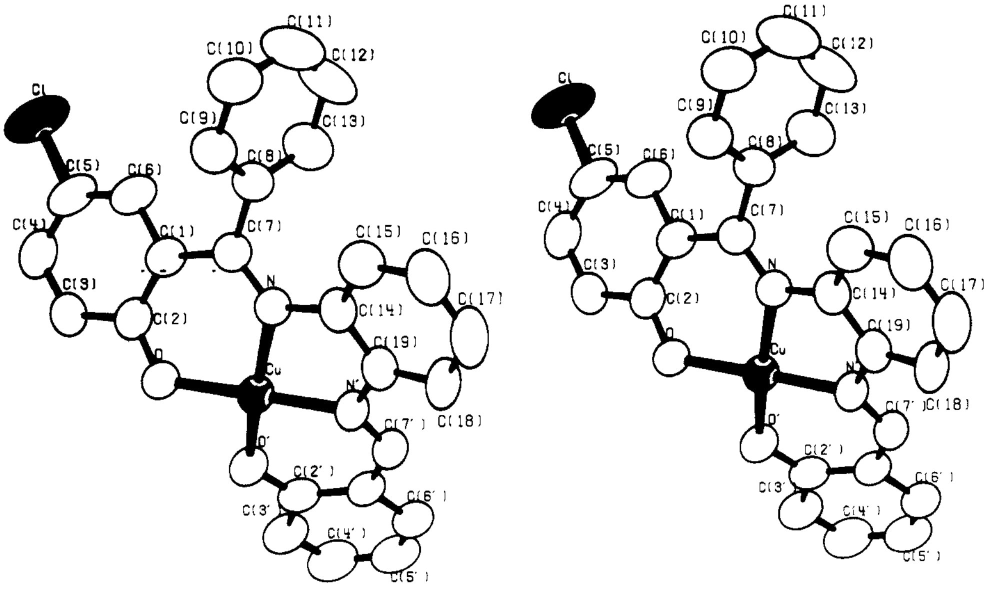

Figure 2. Stereoview of [Cu(CBP-PHEN-5-ClSAL)]·H_2O.

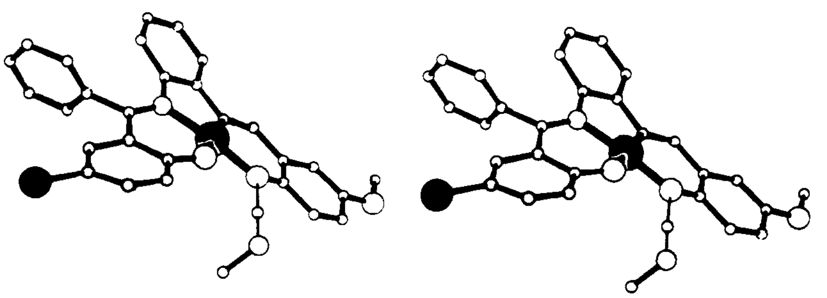

Figure 3. Stereoview of [Cu(CBP-PHEN-5-MeOSAL)]·CH_3OH. Labels are analogous to those of Figure 1.

We have prepared a series of unsymmetrical tetradentate Schiff base ligands from a range of substituted salicylaldehydes. Substituent groups in the 3- and 6-positions provide the possibility of steric hindrance in the chelate ring while a number of different groups in the 5-position allow for the study of possible electronic effects.

Crystal Structures. The final positional parameters for the complexes [Cu(CBP-PHEN-SAL)]·CH_3OH, [Cu(CBP-PHEN-5-ClSAL)]·H_2O, [Cu(CBP-PHEN-5-OCH_3SAL)]·CH_3OH, and [Ni(CBP-PHEN-CBP)] are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the esimated standard deviations, derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1–4 show the four complexes drawn to scale.

Each of the four complexes is mononuclear, but a noteworthy feature is that each of the three copper(II) complexes with un-

Table I. Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
a. [Cu(CBP-PHEN-SAL)]·CH$_3$OH							
Cu	0.4563 (1)	0.29142 (8)	0.30770 (6)	C(11)	0.1893 (9)	−0.3967 (7)	0.1313 (5)
Cl	0.2532 (3)	−0.0711 (2)	−0.2112 (1)	C(12)	0.3382 (9)	−0.3320 (7)	0.1833 (5)
O(1)	0.3919 (6)	0.3280 (4)	0.1808 (3)	C(13)	0.3755 (8)	−0.1904 (6)	0.1957 (5)
O(2)	0.6156 (6)	0.4465 (4)	0.3506 (3)	C(14)	0.2931 (8)	0.0677 (6)	0.3433 (5)
O	0.2920 (9)	0.4597 (6)	0.8049 (5)	C(15)	0.1693 (8)	−0.0312 (7)	0.3382 (5)
N(2)	0.4939 (6)	0.2528 (5)	0.4367 (4)	C(16)	0.1517 (9)	−0.0604 (8)	0.4274 (6)
N(1)	0.3235 (6)	0.1123 (5)	0.2610 (4)	C(17)	0.2483 (10)	0.0076 (8)	0.5181 (5)
C(1)	0.3141 (8)	0.0899 (6)	0.0866 (5)	C(18)	0.3668 (9)	0.1104 (7)	0.5259 (5)
C(2)	0.3523 (8)	0.2345 (6)	0.0954 (5)	C(19)	0.3874 (8)	0.1423 (6)	0.4386 (5)
C(3)	0.3466 (9)	0.2765 (7)	0.0069 (5)	C(1′)	0.7040 (8)	0.4442 (7)	0.5256 (5)
C(4)	0.3126 (8)	0.1884 (7)	−0.0856 (5)	C(2′)	0.7094 (9)	0.4947 (7)	0.4393 (5)
C(5)	0.2873 (8)	0.0460 (7)	−0.0933 (5)	C(3′)	0.8278 (9)	0.6104 (7)	0.4599 (6)
C(6)	0.2886 (8)	−0.0012 (7)	−0.0099 (5)	C(4′)	0.9203 (10)	0.6698 (7)	0.5536 (6)
C(7)	0.2987 (7)	0.0354 (6)	0.1702 (5)	C(5′)	0.9125 (10)	0.6216 (8)	0.6360 (6)
C(8)	0.2587 (8)	−0.1191 (6)	0.1503 (5)	C(6′)	0.8082 (10)	0.5099 (8)	0.6202 (6)
C(9)	0.1089 (8)	−0.1868 (7)	−0.0946 (5)	C(7′)	0.5983 (9)	0.3281 (7)	0.5201 (5)
C(10)	0.0755 (9)	−0.3268 (7)	0.0861 (6)	C	0.2374 (12)	0.5675 (11)	0.8655 (7)
b. [Cu(CBP-PHEN-5-ClSAL)]·H$_2$O							
Cu	0.1593 (2)	0.0894 (5)	0.0895 (1)	C(10)	0.268 (2)	0.171 (5)	0.3498 (11)
Cl	0.6066 (4)	−0.017 (1)	0.2812 (3)	C(11)	0.290 (2)	0.014 (4)	0.3758 (11)
Cl′	−0.1673 (5)	0.467 (1)	−0.1568 (3)	C(12)	0.304 (2)	−0.144 (5)	0.3552 (12)
O	0.274 (1)	−0.012 (3)	0.0899 (6)	C(13)	0.285 (2)	−0.151 (4)	0.2966 (10)
O′	0.150 (1)	0.185 (3)	0.0193 (6)	C(14)	0.084 (1)	0.031 (4)	0.1773 (9)
OX1	0.735 (1)	0.284 (4)	0.5070 (9)	C(15)	0.013 (1)	0.105 (4)	0.1326 (8)
OX2	0.310 (2)	0.406 (6)	0.0311 (14)	C(16)	−0.076 (2)	0.126 (4)	0.1404 (10)
N	0.179 (1)	0.022 (3)	0.1666 (7)	C(17)	−0.089 (2)	0.040 (4)	0.1879 (10)
N′	0.035 (1)	0.148 (3)	0.0862 (7)	C(18)	−0.021 (1)	−0.034 (3)	0.2289 (8)
C(1)	0.339 (1)	0.003 (3)	0.1918 (8)	C(19)	0.065 (1)	−0.053 (4)	0.2216 (8)
C(2)	0.343 (2)	−0.017 (4)	0.1404 (9)	C(1′)	−0.010 (1)	0.266 (4)	−0.0079 (9)
C(3)	0.433 (2)	−0.047 (4)	0.1268 (11)	C(2′)	0.076 (2)	0.244 (4)	−0.0183 (9)
C(4)	0.508 (2)	−0.045 (4)	0.1731 (11)	C(3′)	0.084 (2)	0.305 (4)	−0.0709 (10)
C(5)	0.507 (1)	−0.019 (3)	0.2254 (8)	C(4′)	0.010 (1)	0.370 (4)	−0.1141 (9)
C(6)	0.423 (2)	−0.005 (4)	0.2335 (9)	C(5′)	−0.082 (2)	0.394 (5)	−0.1023 (11)
C(7)	0.254 (1)	0.008 (4)	0.2073 (9)	C(6′)	−0.087 (2)	0.324 (4)	−0.0516 (10)
C(8)	0.265 (2)	0.007 (4)	0.2670 (9)	C(7′)	−0.026 (2)	0.215 (4)	0.0385 (9)
C(9)	0.247 (2)	0.175 (4)	0.2920 (10)				
c. [Cu(CBP-PHEN-5-OCH$_3$SAL)]·CH$_3$OH							
Cu	0.8053 (2)	0.2963 (1)	0.3209 (1)	C(11)	0.363 (2)	−0.356 (1)	0.1952 (10)
Cl	0.1082 (5)	−0.0424 (4)	−0.1489 (3)	C(12)	0.527 (2)	−0.318 (1)	0.2119 (10)
O	0.642 (1)	0.3335 (8)	0.2093 (5)	C(13)	0.586 (2)	−0.182 (1)	0.2199 (8)
O′	0.942 (1)	0.4461 (7)	0.3240 (5)	C(14)	0.737 (1)	0.094 (1)	0.3992 (7)
O(2)	1.586 (1)	0.7233 (8)	0.6060 (6)	C(15)	0.650 (1)	0.001 (1)	0.4271 (7)
O(M)	0.848 (2)	0.5307 (11)	0.1427 (7)	C(16)	0.731 (2)	−0.024 (1)	0.5191 (8)
N	0.672 (1)	0.1319 (8)	0.3076 (5)	C(17)	0.893 (2)	0.043 (1)	0.5889 (7)
N′	0.966 (1)	0.2726 (8)	0.4412 (6)	C(18)	0.976 (1)	0.141 (1)	0.5654 (7)
C(1)	0.472 (2)	0.110 (1)	0.1343 (8)	C(19)	0.897 (1)	0.166 (1)	0.4714 (7)
C(2)	0.518 (2)	0.247 (1)	0.1324 (7)	C(1′)	1.188 (2)	0.460 (1)	0.4806 (7)
C(3)	0.417 (2)	0.293 (1)	0.0464 (8)	C(2′)	1.098 (1)	0.502 (1)	0.3945 (7)
C(4)	0.294 (2)	0.208 (1)	−0.0359 (8)	C(3′)	1.186 (2)	0.612 (1)	0.3787 (8)
C(5)	0.262 (2)	0.069 (1)	−0.0378 (8)	C(4′)	1.341 (2)	0.679 (1)	0.4480 (8)
C(6)	0.350 (2)	0.021 (1)	0.0455 (8)	C(5′)	1.429 (2)	0.644 (1)	0.5389 (8)
C(7)	0.550 (1)	0.059 (1)	0.2235 (7)	C(6′)	1.353 (2)	0.534 (1)	0.5552 (8)
C(8)	0.481 (1)	−0.087 (1)	0.2128 (7)	C(7′)	1.114 (1)	0.347 (1)	0.5025 (8)
C(9)	0.320 (2)	−0.126 (1)	0.1969 (8)	C(8′)	1.683 (2)	0.694 (1)	0.7016 (9)
C(10)	0.255 (2)	−0.264 (1)	0.1860 (9)	C(M)	0.857 (3)	0.429 (3)	0.0765 (14)
d. [Ni(CBP-PHEN-CBP)]							
Ni	0.1394 (1)	−0.0274 (1)	−0.1828 (1)	C(14)	0.0875 (8)	0.1823 (6)	−0.3222 (5)
Cl	0.4244 (3)	−0.3559 (2)	−0.5926 (1)	C(15)	0.0161 (8)	0.2549 (6)	−0.3979 (5)
Cl′	0.5060 (3)	0.0200 (2)	0.2322 (1)	C(16)	−0.0455 (8)	0.3716 (7)	−0.3824 (5)
O	0.1232 (6)	−0.1836 (4)	−0.2164 (3)	C(17)	−0.0312 (9)	0.4159 (8)	−0.2928 (6)
O′	0.1418 (6)	−0.1093 (4)	−0.0467 (3)	C(18)	0.0388 (9)	0.3444 (7)	−0.2160 (5)
N	0.1422 (9)	0.0552 (6)	−0.3218 (5)	C(19)	0.0983 (8)	0.2262 (6)	−0.2300 (5)
N′	0.1565 (6)	0.1334 (5)	−0.1518 (4)	C(1′)	0.2609 (8)	0.0538 (6)	0.0036 (5)
C(1)	0.2310 (8)	−0.1252 (6)	−0.3989 (5)	C(2′)	0.2144 (9)	−0.0713 (7)	0.0165 (5)
C(2)	0.1823 (8)	−0.2128 (6)	−0.3058 (5)	C(3′)	0.2482 (8)	−0.1591 (7)	0.1042 (5)
C(3)	0.1980 (9)	−0.3427 (7)	−0.3114 (5)	C(4′)	0.3308 (9)	−0.1306 (7)	0.1717 (6)
C(4)	0.2699 (8)	−0.3845 (7)	−0.3984 (5)	C(5′)	0.3898 (9)	−0.0096 (8)	0.1494 (6)
C(5)	0.3246 (8)	−0.2987 (7)	−0.4847 (5)	C(6′)	0.3521 (9)	0.0797 (8)	0.0727 (6)
C(6)	0.3043 (8)	−0.1711 (7)	−0.4868 (5)	C(7′)	0.2175 (9)	0.1554 (7)	−0.0753 (5)
C(7)	0.1985 (7)	0.0113 (6)	−0.4075 (5)	C(8′)	0.2491 (9)	0.2877 (7)	−0.0673 (5)
C(8)	0.2292 (8)	0.0972 (6)	−0.5108 (5)	C(9′)	0.3536 (9)	0.3519 (7)	−0.1364 (5)
C(9)	0.3193 (8)	0.1945 (6)	−0.5213 (5)	C(10′)	0.3866 (9)	0.4723 (7)	−0.1276 (6)
C(10)	0.3445 (8)	0.2806 (7)	−0.6138 (5)	C(11′)	0.3093 (9)	0.5279 (8)	−0.0491 (6)
C(11)	0.2755 (9)	0.2713 (7)	−0.6962 (6)	C(12′)	0.2082 (9)	0.4657 (7)	0.1892 (5)
C(12)	0.1863 (9)	0.1745 (7)	−0.6881 (5)	C(13′)	0.1719 (9)	0.3438 (7)	0.0139 (5)
C(13)	0.1636 (9)	0.0862 (7)	−0.5960 (5)				

Table II. Bond Distances and Selected Intermolecular Contacts (Å) for [Cu(CBP-PHEN-SAL)]·CH_3OH (A), [Cu(CBP-PHEN-5-ClSAL)]·H_2O (B), [Cu(CBP-PHEN-5-OCH_3SAL)]·CH_3OH (C), and [Ni(CBP-PHEN-CBP)] (D)

	A	B	C	D
M-O	1.864 (2)	1.892 (7)	1.806 (5)	1.842 (2)
M-O'	1.907 (2)	1.867 (8)	1.842 (4)	1.829 (3)
M-N	1.968 (2)	1.943 (9)	1.886 (5)	1.857 (3)
M-N'	1.898 (2)	1.929 (9)	1.835 (6)	1.878 (3)
O-C(2)	1.305 (3)	1.391 (12)	1.302 (7)	1.297 (4)
O'-C(2')	1.281 (4)	1.307 (12)	1.309 (8)	1.297 (4)
N-C(7)	1.299 (3)	1.293 (11)	1.297 (7)	1.317 (5)
N-C(14)	1.411 (3)	1.555 (13)	1.415 (7)	1.434 (4)
N'-C(19)	1.416 (3)	1.353 (12)	1.452 (7)	1.439 (4)
N'-C(7')	1.332 (4)	1.366 (12)	1.279 (8)	1.302 (4)
O-O(M)	3.319 (5)[a]			
O-O(X1)		2.82 (1)[b]		
O(X1)-O(X2)		2.88 (2)[b]		

[a] Symmetry transformation: $1-x, 1-y, 1-z$. [b] Symmetry transformation: $1-x, y-{}^1/_2, {}^1/_2-z$.

Table III. Bond Angles (deg) for [Cu(CBP-PHEN-SAL)]·CH_3OH (A), [Cu(CBP-PHEN-5-ClSAL)]·H_2O (B), [Cu(CBP-PHEN-5-OCH_3SAL)]·CH_3OH (C), and [Ni(CBP-PHEN-CBP)] (D)

	A	B	C	D
O-M-O	89.95 (9)	87.1 (3)	84.5 (2)	87.3 (1)
O-M-N	92.31 (8)	92.2 (3)	94.6 (2)	92.7 (1)
O-M-N'	172.7 (1)	169.9 (4)	174.0 (3)	178.7 (1)
O'-M-N	169.89 (9)	171.8 (4)	173.6 (2)	178.5 (1)
O'-M-N'	94.9 (1)	95.2 (4)	94.3 (2)	94.0 (1)
N-M-N'	84.0 (1)	87.0 (4)	87.2 (2)	86.1 (1)
M-O-C(2)	124.6 (2)	117.7 (7)	127.3 (4)	122.8 (2)
M-O'-C(2')	127.2 (2)	127.4 (8)	126.6 (4)	122.9 (2)
M-N-C(7)	122.7 (2)	130.3 (8)	123.4 (4)	126.7 (3)
M-N-C(14)	110.8 (2)	107.2 (6)	110.4 (4)	108.9 (2)
M-N'-C(19)	113.1 (2)	114.6 (7)	111.2 (4)	108.3 (2)
M-N'-C(7')	124.6 (2)	120.7 (8)	128.6 (4)	124.9 (3)

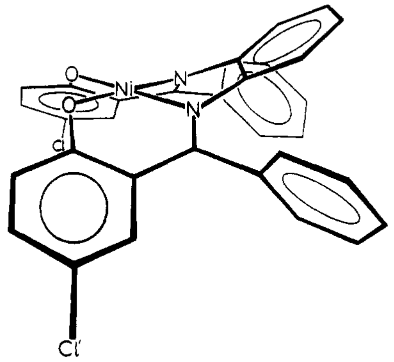

Figure 4. Side view of [Ni(CBP-PHEN-CBP)].

symmetrical ligands crystallizes with a solvent molecule within hydrogen-bonding distance of a ligand oxygen atom. For the complexes of CBP-PHEN-SAL and CBP-PHEN-5-OCH_3SAL, this is methanol while in [Cu(CBP-PHEN-5-ClSAL)] it is water. The nickel(II) complex with the symmetrical ligand CBP-PHEN-CBP crystallizes without any occluded solvent molecules. The metal to donor atom distances do vary for the unequal halves of the unsymmetrical ligands, but the variation is not systematic. For CBP-PHEN-SAL and CBP-PHEN-5-OCH_3SAL, the oxygen bonded more closely to the metal is the one associated with the bulky CBP fragment, while with CBP-PHEN-5-ClSAL, the less bulky 5-ClSAL fragment has the shorter metal to oxygen bond. The irregular variation is not very surprising given the hydrogen bonding of solvent molecules to the phenolic oxygen donor atoms. Even the nickel complex with the symmetrical CBP-PHEN-CBP has a small difference of 0.013 Å between the two chemically equivalent Ni-O bonds. As with the bond distances, the bond angles do not reveal a strong systematic trend between the unequivalent halves of the unsymmetrical ligands.

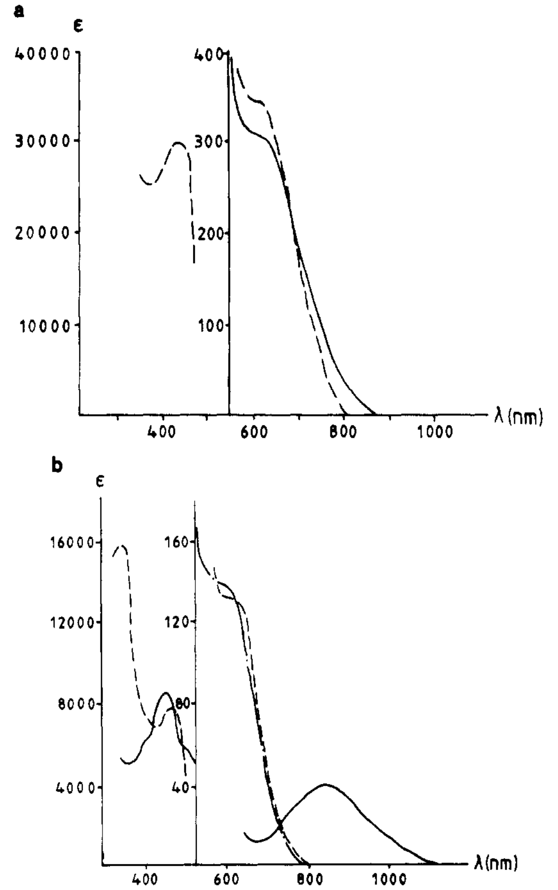

Figure 5. Electronic spectra: (a) [Cu(CBP-PHEN-SAL)] in solid state (—) and in CH_2Cl_2 (---); (b) [Ni(CBP-PHEN-CBP)] in solid state (-·-), in CH_2Cl_2 (---), and in pyridine (—).

There is, however, a marked difference between the two fragments of the unsymmetrical ligands, and this results from the steric constraints imposed by the CBP fragments, but not the substituted SAL. The bulky CBP, with its phenol substituent on the imine carbon, interacts sterically with the phenylenediamine ring; the CBP phenyl ring is rotated roughly perpendicular to the rest of the molecular plane. In addition, the entire fragment bends away from the remainer of the molecule. The greatest part of the bending occurs at the CBP donor atoms. By contrast, the substituted or unsubstituted SAL part of the molecule, having no such steric constraints, remains essentially coplanar with the phenyl ring of *o*-phenylenediamine. The net effect of this bending is to move the CBP oxygen out of the plane formed by the Cu and the remaining three donor atoms. This constitutes, approximately, a distortion toward tetrahedral geometry.

The distortion of the ligands is shown most dramatically in the [Ni(CBP-PHEN-CBP)] complex, seen from the side in Figure 4 to show this. Here, the two ligand fragments OCCCN bonded to Ni are inclined at a 57.6° angle to each other. However, the metal atom remains inside the undistorted donor atom plane O_2N_2: none of the five atoms Ni, O, O', N, or N' deviate more than 0.1 Å from this plane.

Copper(II) Complexes. The room-temperature magnetic moments of the copper(II) complexes (Table IV) fall in the range 1.78–1.94 μ_B. These values are consistent with the expected monomeric structures of the complexes. The d-d spectra of the complexes (Table IV; Figure 5a) are present as a shoulder at 610–660 nm (ϵ = 300–500) of an intense UV band at 410–440 nm. These spectra are similar to those[22] for copper(II) complexes of bidentate Schiff base ligands that have been shown to contain square-planar copper(II) atoms by X-ray crystallography. The

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[22] Chia, P. C.; Freyberg, D. P.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1976**, *16*, 254.

Table IV. Room-Temperature Magnetic Moments

L^{2-}	complex	μ_B	temp, K
CBP-PHEN-SAL	CuL	1.85	301.0
	$NiL\cdot {}^1/_2H_2O$	0.41	300.6
	$NiL\cdot(py)_2$	3.27	291.6
CBP-PHEN-NAP	CuL	1.85	300.1
	NiL	0.51	300.0
CBP-PHEN-5-ClSAL	$CuL\cdot {}^1/_2H_2O$	1.89	294.2
	NiL	0.71	294.2
CBP-PHEN-5-BrSAL	$CuL\cdot {}^1/_2H_2O$	1.86	301.0
	NiL	0.97	301.0
CBP-PHEN-5-MeOSAL	$CuL\cdot 2H_2O$	1.88	294.7
	NiL	0.95	294.6
CBP-PHEN-4-MeOSAL	$CuL\cdot {}^1/_2H_2O$	1.85	294.6
	$NiL\cdot {}^1/_2H_2O$	0.89	294.6
CBP-PHEN-3-MeOSAL	$CuL\cdot CH_3OH$	1.78	297.9
	NiL	1.03	297.9
CBP-PHEN-3-EtOSAL	CuL	1.89	297.7
	$NiL\cdot H_2O$	0.47	297.9
CBP-PHEN-4,6-MeO_2SAL	$CuL\cdot H_2O\cdot {}^1/_2CH_2Cl_2$	1.83	290.8
	$NiL\cdot 2H_2O$	1.01	290.6
CBP-PHEN-PYRR	$CuL\cdot H_2O$	1.94	290.7
	NiL	0.77	292.6
CBP-PHEN-CBP	NiL	0.89	292.0

spectra of the complexes are similar in the solid state, in dichloromethane, and in pyridine solutions, indicating a square-planar environment in each solution. The spectra indicate that the solid-state structures are similar to the solution structures, but they are not expected to be identical because the solid-state structures are known to be influenced by the hydrogen-bonded solvent molecules occluded in the crystals and by packing effects.

The spectra of all the complexes are similar despite the changes of position and nature of the salicylaldehyde substituents. This is not surprising since the d–d bands occur as a shoulder on the intense UV band, which can be expected to obscure changes in the d–d band positions brought about by small changes in the environment of the copper atoms.

As with the symmetrical ligand analogues,[23] the copper complexes with the unsymmetrical ligands form binuclear and polynuclear complexes.[24] These differ markedly and interestingly from those of the symmetrical ligand analogues, but the bi- or polynucleation still involves bridging via the phenolic oxygens of the ligands. Cu(CBP-PHEN-Im) differs from the others in having only one phenolic oxygen and is sterically unable to form analogous strong bonds to metal diketonates. However, it has the outer nitrogen of the deprotonated imidazole fragment pointing away from the steric bulk of the ligand, available for complex formation, **8**. Adduct complexes form readily, and the derivatives with $M(hfa)_2$ (M = Cu(II), Co(II)) were formed to verify this.[25] As expected, Cu(CBP-PHEN-PYRR) does not form adduct complexes of this type.

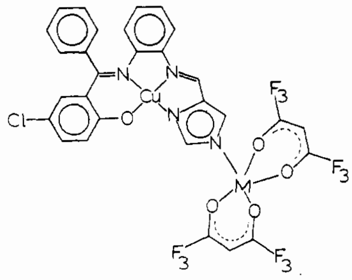

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Table V. UV–Visible–Near-Infrared Spectra (nm)

L^{2-}	solid state	CH_2Cl_2[a–c]	py[a–c]
(a) Copper Complexes			
CBP-PHEN-SAL	650 (sh)	390 (sh)	390 (sh)
		430 (14 600)	435 (17 300)
		620 (sh)	650 (sh)
CBP-PHEN-NAP	650 (sh)	435 (19 500)	435 (20 000)
		625 (sh)	500 (sh), 680 (sh)
CBP-PHEN-5-ClSAL	625 (sh)	390 (sh)	390 (sh)
		438 (16 500)	440 (15 800)
		625 (sh)	650 (sh)
CBP-PHEN-5-BrSAL	650 (sh)	390 (sh)	390 (sh)
		430 (22 000)	440 (16 500)
		625 (sh)	650 (sh)
CBP-PHEN-5-MeOSAL	650 (sh)	440 (9400)	450 (10 000)
		650 (sh)	660 (sh)
CBP-PHEN-4-MeOSAL	610 (sh)	414 (23 700)	420 (16 900)
		615 (sh)	640 (sh)
CBP-PHEN-3-MeOSAL	650 (sh)	440 (13 400)	440 (9000)
		635 (sh)	630 (sh)
CBP-PHEN-3-EtOSAL	650 (sh)	360 (sh)	
		440 (18 600)	440 (15 900)
		640 (sh)	650 (sh)
CBP-PHEN-4,6-MeO_2SAL	625 (sh)	375 (26 200)	375 (22 890)
		425 (sh)	410 (21 000)
		610 (sh)	625 (sh)
CBP-PHEN-PYRR	630 (sh)	420 (500)	420 (27 500)
		630 (sh)	640 (sh)
(b) Nickel Complexes			
CBP-PHEN-SAL	600 (sh)	350 (8700)	415 (sh)
		470 (4300)	450 (19 000)
		600 (sh)	550 (sh), 850 (77)
CBP-PHEN-NAP	610 (sh)	385 (24 300)	400 (sh)
		450 (9200)	445 (16 300)
		485 (9300)	500 (sh)
		590 (sh)	815 (92)
CBP-PHEN-5-ClSAL	575 (sh)	380 (17 000)	415 (sh)
		475 (6200)	450 (8900)
		590 (sh)	500 (sh), 800 (85)
CBP-PHEN-5-BrSAL	590 (sh)	380 (21 000)	415 (sh)
		470 (8800)	450 (14 000)
		590 (sh)	845 (78)
CBP-PHEN-5-MeOSAL	610 (sh)	385 (20 000)	390 (sh)
		460 (6600)	455 (9300)
		610 (sh)	510 (sh), 850 (30)
CBP-PHEN-4-MeOSAL	585 (sh)	380 (26 500)	415 (sh)
		460 (12 500)	435 (17 100)
		590 (sh)	490 (sh), 810 (sh)
			840 (60)
CBP-PHEN-3-MeOSAL	600 (sh)	375 (18 800)	425 (sh)
		470 (7200)	450 (14 300)
		600 (sh)	500 (sh), 800 800 (58)
CBP-PHEN-3-EtOSAL	630 (sh)	375 (22 000)	
		470 (8100)	450 (14 000)
		590 (sh)	820 (48)
CBP-PHEN-4,6-MeO_2SAL	600 (sh)	380 (28 000)	380 (26 000)
		460 (15 000)	410 (24 000)
		580 (sh)	440 (22 000)
			830 (54)
CBP-PHEN-PYRR	530 (sh)	440 (31 800)	440 (16 600)
		530 (sh)	530 (sh)
CBP-PHEN-CBP	610 (sh)	370 (15 500)	415 (sh)
		460 (10 700)	450 (10 000)
		610 (sh)	540 (sh), 850 (50)

[a] Extinction coefficient in parentheses. [b] Visible spectra, 0.01 M. [c] UV spectra, 0.0002 M.

Nickel(II) Complexes. The room-temperature magnetic moments are in the range 0.41–1.03 μ_B (Table IV), indicating the presence of low-spin nickel(II). The small deviations from dia-

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magnetism are possibly due to the presence of small amounts of paramagnetic impurities.

The d–d spectra of the complexes (Table V; Figure 5) in the solid state and in dichloromethane solution consist of a shoulder at 550–630 nm on the side of an intense (ϵ = 4000–13 000) UV band at 460–490 nm. This type of spectrum is characteristic of low-spin square-planar nickel(II) Schiff base complexes.[26] The d–d bands are present as shoulders on the intense UV band so it is difficult to observe any shifts that different salicylaldehyde substituents might produce on these bands. Ni(CBP-PHEN-PYRR) does, however, appear to have the d–d bands at lower wavelength (530 nm), indicating a stronger ligand field than the other complexes.

When the complexes, Ni(CBP-PHEN-XSAL), are dissolved in pyridine, the spectra change, with a new band appearing at 800–850 nm (ϵ = 30–90). This band is consistent with the presence of high-spin six-coordinate nickel(II).

$$\mathrm{NiL} + 2\mathrm{py} \rightarrow \mathrm{NiL}\cdot(\mathrm{py})_2$$

The extinction coefficients of this band are higher than those usually observed for octahedral nickel(II) (ϵ = 5–20), and this may be due to the lower symmetry of these complexes. In the case of Ni(CBP-PHEN-4-MeOSAL), this band is split into two components, which is also indicative of lower symmetry.

When Ni(CBP-PHEN-SAL) is recrystallized from pyridine, the high-spin complex, $\mathrm{NiL}\cdot(\mathrm{py})_2$ is isolated. The isolation of the complex confirms the deduction of adduct formation from the pyridine solution spectra. The adducts probably have a trans octahedral structure. This behavior, in pyridine solution, is much simpler than that reported[27,28] for the similar symmetrical complex Ni(SAL-PHEN-SAL) where conflicting evidence has been given as to whether or not pyridine coordinates to the complex in pyridine solution. No paramagnetic pyridine adduct of this complex has been isolated.

When Ni(CBP-PHEn-PYRR) is dissolved in pyridine, the spectrum obtained is similar to that in dichloromethane solution, indicating no adduct formation. The complex also crystallizes unchanged from pyridine solution. Apparently, the stronger ligand field, as indicated by the higher energy of the d–d bands, is sufficient to prevent adduct formation.

Conclusion. A facile synthesis has been developed for the production of an entire class of unsymmetrical Schiff base ligands. The unsymmertical ligands used here are tetradentates with bulky substituents on one side of the Schiff base. The complexes differ markedly from the unsubstituted parent complexes and from the symmetrical analogues with equivalent bulky substituents on both sides. Except for different peripheral substituents, the various unsymmetrical ligands resemble each other sterically and form similar complexes. The variation of the core coordination structures in the solid state is small and nonsystematic. The solid-state structures are governed by solid-state effects, especially by the hydrogen bonding with the occluded solvent molecules. The specific effects of the unsymmetrical benzophenone salicylaldimine based ligands on the metal coordination is a partial but irregular distortion toward tetrahedral geometry, accompanied by a marked distortion of the molecular plane. This allows the metal geometry to be varied, as with some other ligands used for modeling metal geometries in biomolecules, though the most useful biological modeling is expected to be in binuclear complexes formed from unsymmetrical ligands with oxygen and imidazole ligands. The way that the unsymmetrical coordination and the consequent distortion influences the formation of new types of bi- and polynuclear complexes will be reported subsequently.

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Registry No. HCBP, 85-19-8; HCBP-PHEN, 94070-52-7; HCBP-PHEN-SALH, 94070-53-8; HCBP-PHEN-5ClSALH, 94070-54-9; HCBP-PHEN-5BrSALH, 94070-55-0; HCBP-PHEN-5MeOSALH, 94070-56-1; HCBP-PHEN-4MeOSALH, 94070-57-2; HCBP-PHEN-3MeOSALH, 94070-58-3; HCBP-PHEN-3EtOSALH, 94070-59-4; HCBP-PHEN-4,6DiMeOSALH, 94070-60-7; HCBP-PHEN-NAPH, 94070-61-8; $\mathrm{Cu(nfa)_2}$, 14781-45-4; $\mathrm{Co(hfa)_2}$, 196488-3-0; Cu(CBP-PHEN-SAL)·MeOH, 94089-92-6; Ni(CBP-PHEN-SAL), 94089-93-7; Cu(CBP-PHEN-NAP), 94070-62-9; Ni(CBP-PHEN-NAP), 94070-63-0; Cu(CBP-PHEN-5ClSAL)·$\mathrm{H_2O}$, 94070-64-1; Ni(CBP-PHEN-5ClSAL), 94070-65-2; Cu(CBP-PHEN-5BrSAL), 94070-66-3; Ni(CBP-PHEN-5BrSAL), 94070-67-4; Cu(CBP-PHEN-5MeOSAL), 94070-69-6; Ni(CBP-PHEN-5MeOSAL), 94070-70-9; Cu(CBP-PHEN-4MeOSAL), 94070-71-0; Ni(CBP-PHEN-4MeOSAL)·$\mathrm{H_2O}$, 94070-72-1; Cu(CBP-PHEN-3MeOSAL), 94070-73-2; Ni(CBP-PHEN-3MeOSAL), 94070-74-3; Cu(CBP-PHEN-3EtOSAL), 94070-75-4; Ni(CBP-PHEN-3EtOSAL), 94070-76-5; Cu(CBP-PHEN-4,6DiMeOSAL), 94070-77-6; Ni(CBP-PHEN-4,6DiMeOSAL), 94070-78-7; Cu(CBP-PHEN-PYRR), 94070-79-8; Ni(CBP-PHEN-PYRR), 94070-80-1; Ni(CBP-PHEN-CBP), 94070-81-2; Ni(CBP-PHEN-SAL)·2py, 94070-82-3; Cu(CBP-PHEN-Im), 94070-83-4; pyrrole-2-carbaldehyde, 1003-29-8; 4(5)-formylimidazole, 3034-50-2; 4(5)-(hydroxymethyl)imidazole, 822-55-9; benzoyl chloride, 98-88-4; 4-chlorophenol, 106-48-9; 1,2-diaminobenzene, 95-54-5.

Supplementary Material Available: Listings of positional and thermal parameters, distances, angles, microanalytical data, least-squares planes, and observed and calculated structure factors (53 pages). Ordering information is given on any current masthead page.

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