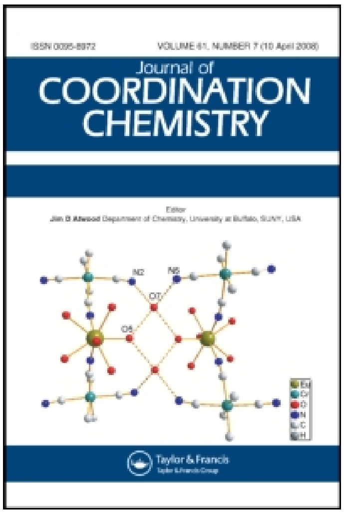

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A SPECTRAL STUDY OF Cu^{2+} AND Cd^{2+} WITH A SUBSTITUTED PYRAZINE LIGAND

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We wish to report a novel ligand that forms an intense blue to purple color when complexed with various non-transition as well as transition metals. This color appears when Cd^{2+}, Zn^{2+}, Ag^{1+}, Mg^{2+} Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, or Mn^{2+} is added to *N,N′*-bis(4-*N″,N″*-dimethylanilinyl)-2,5-bis(methylenimino)pyrazine (Figure 1) which is dissolved in dimethylformamide (DMF). The ligand is capable of being multidentate; therefore, spectrophotometric titration experiments were performed using Cd^{2+} in one experiment and Cu^{2+} in another experiment. If these ions can be considered as being representative of the non-transition and transition complexes respectively, then the stoichiometry is 1:1 and 2:1 (metal:ligand). Whether this sampling is truly representative is under further investigation.

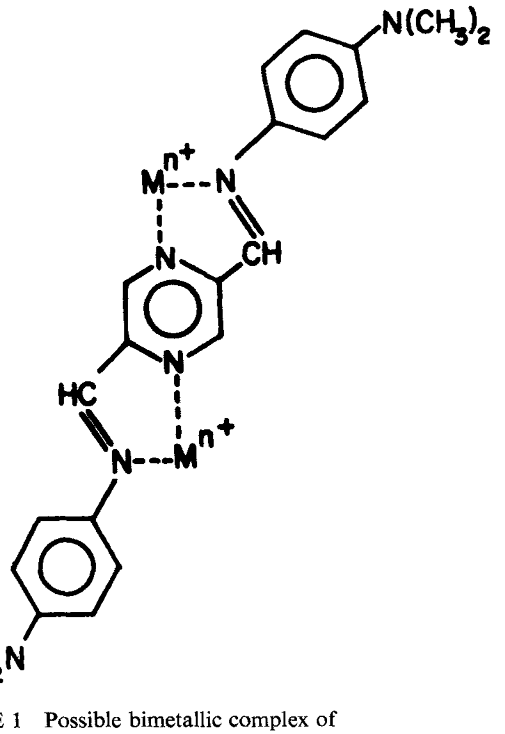

FIGURE 1 Possible bimetallic complex of *N,N′*-bis(4-*N″,N″*-dimethylanilinyl)-2,5-bis(methylenimino)-pyrazine as indicated from spectrophotometric titration.

EXPERIMENTAL SECTION

The synthesis of the *N,N′*-dioxide of *N,N′*-bis(4-*N″,N″*-dimethylanilinyl)-2,5-bis(methylenimino)pyrazine (Figure 2) has been previously described.[1] The melting point, n.m.r., and i.r. spectra we obtained for this compound are as follows:

m.p. = 245–247°C.

n.m.r. ($CDCl_3$, τ)—0.53 (imine), 1.77 (pyrazine), (2.10, 2.25, 3.17, 3.33 (phenyl)), 6.92 (CH_3).

i.r. (nujol, cm^{-1})—2340 (w), 1595 (s), 1530 (s), 1520 (s), 1440 (s), 1360 (s), 1345 (s), 1225 (m), 1180 (s), 1160 (s), 1120 (w), 1070 (s), 1010 (m), 940 (m), 920 (w), 870 (w), 820 (s), 805 (s), 805 (w), 795 (m), 730 (w).

The unusual ligand was obtained when the *N,N′*-dioxide was dissolved in 6N HCl and 2-(2-aminoethyl)-pyridine was added dropwise. A red precipitate resulted that from the analysis, melting point, n.m.r., and i.r. indicated a new compound had been obtained which is best described as the deoxygenated species shown in Figure 1. This new compound showed the remarkable color change when the metal ions were added, whereas the *N,N′*-dioxide did not.

m.p. = 275–277°C.

n.m.r. ($CDCl_3$, τ)—0.47 (imine), 1.17 (pyrazine), (2.40, 2.57, 3.08, 3.23 (phenyl)), 6.95 (CH_3).

i.r. (nujol, cm^{-1})—2320 (w), 1615 (s), 1570 (s), 1555 (shoulder), 1540 (w), 1505 (s), 1455 (s), 1360 (s), 1340 (s), 1295 (w), 1225 (m), 1195 (w), 1175 (s), 1150 (s), 1120 (w), 1060 (m), 1020 (s), 945 (s), 920 (w), 855 (m), 810 (s), 795 (m), 745 (w), 715 (w).

Analysis: Calcd.—C, 70.94; H, 6.49; N, 22.56.
Found—C, 70.46; H, 6.34; N, 22.42.

The experiment was repeated using pyridine instead of 2-(2-aminoethyl)-pyridine to precipitate the deoxygenated species. This time a reddish-orange precipitate resulted that from the analysis, n.m.r., and i.r. indicated once again the deoxygenated species had been obtained. However, the melting point was greatly different from that of the red deoxygenated compound. Also, there was a slight difference in the i.r. and n.m.r. spectra of the two deoxygenated compounds.

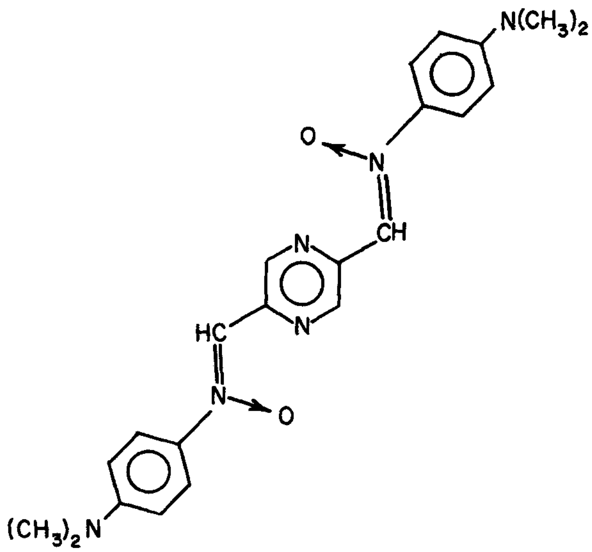

FIGURE 2 *N*,*N*′-bis(4-*N*″,*N*″-dimethylanilinyl)-*N*,*N*′-dioxide-2,5-bis(methylenimino)pyrazine.

m.p. = 251–255°C.

n.m.r. ($CDCl_3$, τ)—0.72 (imine), 1.38 (pyrazine), (2.71, 2.83, 3.25, 3.40 (phenyl)), 7.00 (CH_3).

i.r. (nujol, cm^{-1})—2320 (w), 1650 (m), 1610 (s), 1550 (shoulder), 1500 (s), 1440 (s), 1355 (s), 1340 (shoulder), 1320 (shoulder), 1290 (shoulder), 1220 (m), 1190 (w), 1170 (s), 1150 (s), 1110 (w), 1055 (w), 1010 (s), 940 (s), 850 (w), 810 (s), 790 (m), 710 (w).

Analysis: Calcd.—C, 70.94; H, 6.49; N, 22.56.
Found—C, 70.04; H, 6.25; N, 22.59.

This isomeric compound also showed the color change upon addition of the various metal ions.

Spectrophotometric titrations were accomplished by adding small increments of the metal ion to a solution of the ligand contained in a specially designed cuvette and then correcting the concentrations and absorbances for dilution. Since the ligand is insoluble in water, DMF was chosen as the solvent for metal complex studies. It was discovered that the copper complex was unstable to oxygen over the time period of the experiment. Therefore, all solutions were deaerated with nitrogen, the spectrophotometric cell was flushed with nitrogen, and solutions were transferred via a 2 cc capacity syringe. The cadmium complex decomposed very slowly. No noticeable decomposition occurred over a 24 hr period, but the color disappeared after several weeks of standing in the cuvette. Therefore, no precautions were made while running this titration. $CuSO_4 \cdot 5H_2O$ and $Cd(ClO_4)_2 \cdot 6H_2O$ were used for the experiments. The spectra were taken on a Cary recording spectrophotometer.

RESULTS AND DISCUSSION

The differences between the red and orange deoxygenated species are explained by cis-trans isomerization due to the imine bonds present in the ligand. It is believed that the high melting isomer is in the trans configuration since the melting point can be used as a criteria for choosing between cis-trans isomers.[2] This conclusion is reinforced by the location of the imine proton resonance. The proton in the trans isomer should resonate down field with respect to the imine proton of the cis isomer.[3]

Figure 3 shows the curves obtained from the spectrophotometric titrations. From the slope of a plot of $\log\left[\frac{OD_1 - OD}{OD - OD_2}\right]$ versus $\log\,[M^{n+}]$ one can obtain the metal to ligand stoichiometry,[4] where OD_1 is the optical density obtained by multiplying the analytical concentration of metal by the extinction coefficient of the complex, OD_2 is the optical density given by multiplying the extinction coefficient of the ligand times the analytical concentration of the ligand, and $[M^{n+}]$ is the metal ion concentration. The intercept of such a plot determines $\log \frac{1}{K_f}$, where K_f is defined by $\frac{[M_mL\ ]}{[M^{n+}]^m[L]}$.

When the above analysis was performed for the Cd^{2+} titration the slope was found to be 1.0 and K_f was evaluated as 3.3×10^2. A similar analysis for the Cu^{2+} titration yielded a slope close to 2.

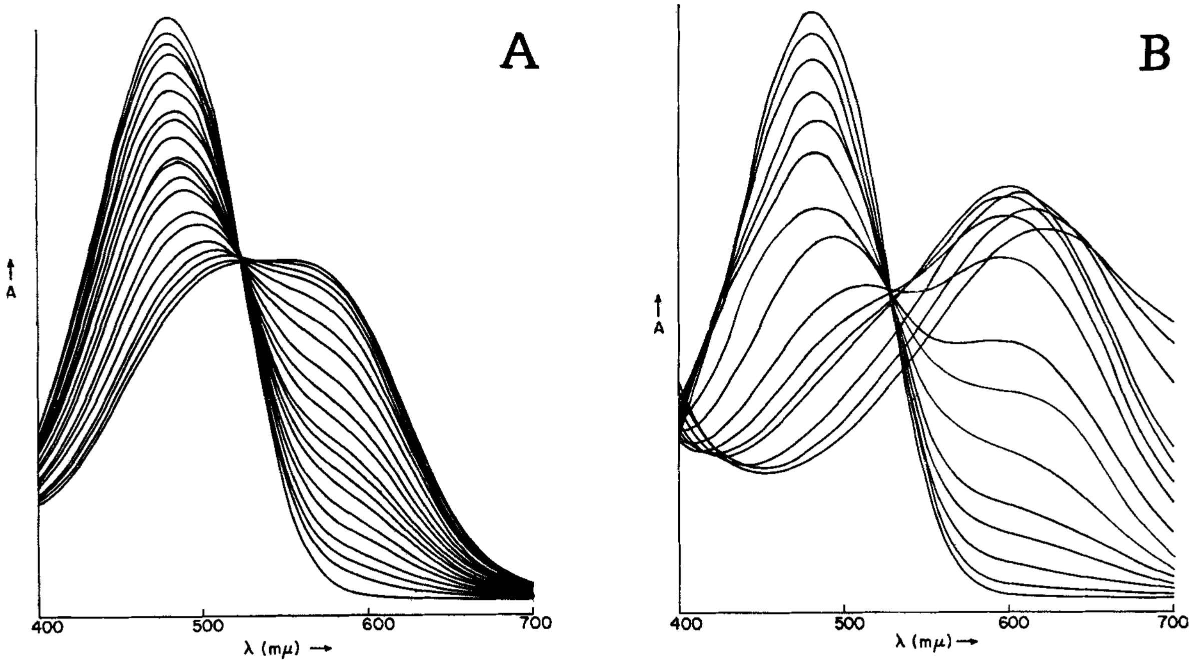

FIGURE 3 (a) Spectrophotometric titration of *N,N'*-bis(4-*N''*,*N''*-dimethylanilinyl)-2,5-bis(methylenimino)-pyrazine with $Cd(ClO_4)_2$. (b) Spectrophotometric titration with $CuSO_4$.

(Due to the apparent formation of another species in the vicinity of 770 mμ (cf. Figure 3b) it was difficult to determine OD_l precisely. The actual slope varies between 2.1 and 2.5 as OD_l varies between 1.1 and 1.0). The value of the formation constant is $K_f = \frac{[Cu_2L^{4+}]}{[Cu^{2+}]^2[L]} = 2.5 \times 10^7$.

It is interesting to speculate that the reason for the 2:1 stoichiometry of the Cu^{2+} complex is due to the ability of copper to donate its "d" electrons to the pyrazine ring. This back-bonding would then increase the basicity of the second nitrogen on the pyrazine ring. Such an effect has been reported for the pentammineruthenium(II)pyrazine complex.[5, 6] This synergistic effect has not been observed for Cd^{2+}, Zn^{2+}, or Hg^{2+} and would explain why the stoichiometry for the Cd^{2+} complex is only 1:1.

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